İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

CORROSION BEHAVIOR OF POLYPYRROLE COATED ALUMINUM SUBSTRATES

M.Sc. Thesis by

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Department : Polymer Sci. and Tech. Program

Programme: Polymer Sci. and Tech. Program

Supervisor : Prof. Dr. Figen Kadırgan

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May 2002 Özgür Eylem Pıtırlı

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LIST OF ABBREVIATIONS

ECP	**:** Electroactive Conducting Polymer
ICP	**:** Instrinsically Conducting Polymer
CR	**:** Corrosion Rate
EIS	**:** Electrochemical Impedance Spectroscopy
SEM	**:** Scanning Electron Microscopy
PPy	**:** Polypyrrole
Py	**:** Pyrrole
1Mpy	**:** 1-Methylpyrrole
NLSF	**:** Non-linear Least Square Fitting
GPN	**:** Gross National Product
OCP	**:** Open Circuit Potential
DC	: Direct Current
AC	: Alternative current
GA	: Galvanic Activation
pTS	: paraToluene**S**ulphonic**A**cid

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Corrosion Behavior of Polypyrrole Coated Aluminum Substrates

Summary

In this study aluminum 6063 substrates are coated by adhesive and homogeneous poylpyrrole film that doped by oxalic acid with two step electrochemical reactions. Several attempts were made to prepare para-toluenesuphonic acid doped polypyrrole films with the same conditions but results were unsuccessfully heterogenous films.

Thereafter the effect of corrosion inhibition of the film in 0.1 M KCl media is examined by polarization curves, EIS and SEM methods. Comparations with bare and chromate treated aluminum substrates have been made. Good corrosion protection has been observed by conducting PPy films. Also different protection characterstics of conducting polymers and chromate layers are noted.

Polypirol Kaplı Alüminyum Parçaların Korozyon Davranışının İncelenmesi

Özet

Çalışmada alüminyun 6063 alaşımı parçalar oksalik asit doplu iletken polypirol ile kaplandı. Bu kaplamalar iki adımlı elektrokimyasal yöntemle yapıldı ve homojen ve iyi yapışmış kaplamalar elde edildi Aynı şartlarda paratoluen sulfonik asitte denenmesine rağmen elde edilen kaplamalar heterojen dolayısıyla uygun olmayan kaplamalardı.

Kaplamadan sonra filmin korozyon koruması 0.1 M KCl ortamında polarizasyon eğrileri, impedand spektroskopisi ve taramalı elektron mikroskobuyla incelendi. Çıplak Al ve kromat kaplı Al yüzeyleri ile karşılaştırmalar yapıldı. Filmin korozyon koruması sağladığı gözlendi. Ayrıca iletken polimerlerin ile kromat yüzeyler arasında ki koruma karakteristiği farkıda gözlendi.

1. INTRODUCTION

Conductive polymers are wide and intense research area both theoretically and experimentally because of their academically interesting structures and promising practical applications like electrodes in batteries, a gas separating membranes, microelectronic devices, microwave absorbants etc. One of the these applications is the corrosion protection that is all time very active subject of study and it is gaining more importance day by day while sources of earth are being exhausted.

Aluminum and its alloys are one of the most widely used commodity materials so their loss by corrosion is economically harmful. In order to control of Al and its alloys corrosion chromate surface treatments and chromate containing epoxy primers are often used. Unfortunately Cr(VI) has been shown to be hazardous to the enviroment and to human health, its use in many countries will be sharply curtailed in the coming years. Electroactive conducting polymers represent a class of interesting materials currently being studies as corrosion control coating an alternative for Cr(VI) based coatings. The electroactivity and the electronic conductivity of these polymers set them apart form traditional organic coatings. Thus, as with chromate, interesting and potentially benefical interactions of conductive polymers with active metal alloys are anticipated.

In this study polypyrrole is used as conducting polymer because of all of the known conducting polymers, polypyrrole is the most frequently used in commercial applications due to the long term stability of its conductivity and possibility of forming homopolymers and composites with improved mechanical properties. It's conductivity is establised by oxalic acid doping.

This study concerns with corrosion protection of oxalic acid doped polypyrrole coatings with galvanic activation pretreatment on aluminum 6063 alloy substrates. Corrosion examined by electrochemical impedance, polarisation curves and scanning electron microscope studies (SCE) in aggressive Cl^- enviroments. These coatings are compared with bare and chromate treated substrates. Considerable corrosion protection of this alloy is observed by this coating.

2.THEORETICAL PART

2.1. CORROSION

2.2.1. Corrosion Basics

Corrosion is destructive phenomena that affect all metals. It refers to the loss or conversion into another insoluble compound of the surface layers of the solid in contact with fluid. The solid is normally metal but the term corrosion is also used to refer to the dissolution of ionic crystals or semiconductors. In context of our thread corrosion of metals in contact with aqueous solution at normal temperatures is of predominant interest.

It is estimated that usually it causes damage costs 3% - 5% of the GNP for an industrialized country [1]. Owing to the tremendous economic damage it can cause, corrosion has and continues to be the subject of extensive study especially with a view to its minimization at acceptable expense, both economic and environmental.

Mainly corrosion processes are electrochemical processes. The surface of the corroding metal acts as a mixed electrode, upon which coupled anodic and cathodic reactions take place. At anodic sites, metal atoms pass into solution as positively charged ions (anodic oxidation) the corrosion of a metal in contact with an aqueous solution can be represented by generic half reaction

$$M \longrightarrow M^{n+}(aq) + ne^{-} \qquad 2.1$$

in order to establish corrosion reaction these electrons must be consumed in cathodic sites such as

- in acid environment

$$O_2 + 4H^{+}(aq) + 4e^{-} \longrightarrow 2H_2O \qquad 2.2$$

and / or

$$2H + 2e^{-} \longrightarrow H_2 \qquad 2.3$$

- in alkaline environment

$$O_2 + 2H_2O + 4e^{-} \longrightarrow 4OH^{-} \qquad 2.4$$

and / or

$$2H_2O + 2e^{-} \longrightarrow H_2 + 2OH^{-} \qquad 2.5$$

the metal ions can react immediately with OH^{-} to form insoluble oxides / hydroxides that cover the metal surface, or the metal ion can be released to bulk solution. The reactions that occur depend on pH in the vicinity of the metal surface.

2.1.2. Corrosion Of Aluminum

Aluminum owes its corrosion resistance to the barrier oxide film that forms immediately in a wide variety of environments. Its structure and chemical composition depends on the environmental conditions. This oxide film is self-renewing and accidental abrasion or other mechanical damage of the surface film is rapidly repaired. The conditions that promote corrosion of aluminum and its alloys, therefore, must be those that continuously abrade the film mechanically or promote (electro-)chemical conditions that locally degrade the protective oxide film and minimize the availability of oxygen to rebuild it. The structure of this film consists of two parts. First thin non-porous barrier, second a thick porous layer [2] (Figure2.1).

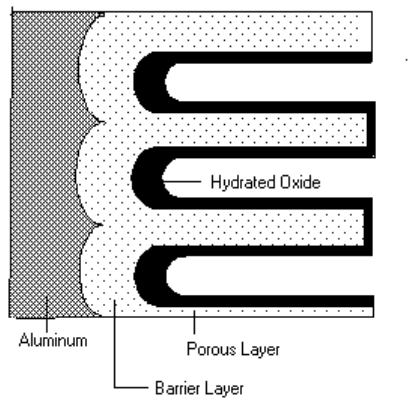


Figure 2.1 Schematic representation of the oxide layer on aluminum

On the other way the presence of the aggressive ions like chloride, create extensive localized attack that is observed as pitting corrosion. Various mechanisms have been proposed to explain the breakdown of passive film in presence of chloride ions, but mechanism is not fully understood. One of them takes into account the migration of the chloride ions to through film. Breakdown occurs when chlorides reach the metal-film interface. But experiments with using radioactive labeled chloride and XPS method, has shown that chlorides does not enter the oxide film but they are chemisorbed onto the oxide surface, first 10-15 A^o of oxide/solution interface, and acts as a reaction partner, aiding dissolution via the formation of oxide-chloride complexes [3,4]. Generally localized corrosion can be prevented by the action of absorptive inhibitors, which prevent the adsorption of the aggressive anions of by the formation of a more resistant oxide film on the metal surface.

Chromates are recognized as being very efficient to inhibit the corrosion of aluminum and aluminum alloys. The action is linked firstly to the formation of an insoluble chromium oxide Cr_2O_2, which strengthens the alumina layer and secondly to the incorporation of chromate ions in the alumina film which prevents pitting corrosion through its ability to repair defects in oxide film. Nevertheless, the toxicity of chromates has led to interests in the use of more environmentally acceptable treatment. One of the alternatives is electroactive conducting polymers (ECPs) that is going to be explained in proceeding chapters.

2.1.3. Measurement of Corrosion

We can classify the measurements two main categories; direct analytical methods, such as weight loss measurements or solution analysis of solution by spectrographic measurements, require relatively long exposure times of the corroding systems. Moreover, these direct methods are in general restricted to systems, which do not form adherent layers of corrosion products. Second one is electrochemical methods, because of electrochemical nature of the corrosion process; different electrochemical measurement techniques have been applied to corrosion systems in order to determine the corrosion rate. The great advantages of electrochemical methods are relatively short measuring time, a high accuracy and possibility of continuous corrosion monitoring. On the other hand, a main disadvantage of all electrochemical method is the necessary perturbation of the corroding system by an externally imposed polarization, which lead to inevitable changes of the system, specific properties such as surface structure and roughness, the adsorption and absorption of hydrogen, the formation of surface layers, sorption process of inhibitors, etc. Furthermore, all electrochemical methods are fitting procedures, presuming more of less knowledge of the kinetics and mechanisms of the reaction occurring in the corroding system.

All electrochemical methods are based on Faraday's law relating the mass flux per unit area and time with current flux. If the current caused by the electron flow could be measured at all, the measured quantity, I_{net} would represent a net effect of the partial currents resulting from oxidation and reduction. I_{net} is generally zero, i.e. for the situation where a metal corrodes due to an oxidation reaction of the metal and one (O_2-reduction) or two simultaneous reduction reactions (O_2-reduction and H_2-evolution) occurring on the same metal. The corrosion rate CR is then proportional to the sum of the partial anodic currents (corrosion current) causing metal dissolution.

$$I_{net} = \sum I_{ox} - \sum |I_{red}| \qquad 2.6$$

CR is defined as the loss of the corroding metal in micrometers per year (μm/a) and can be calculated by:

$$CR = \frac{i_{corr}.t_a.M_{metal}}{zF.d_{metal}}.10^6 \qquad 2.7$$

where i_{corr} corrosion current density (A/m^2), t_a year in seconds (31557600 s), M_{metal} molar weight of the metal (for aluminum 0.0269815 kg/mol), z number of electrons (for Al z = 3), F Faraday constant (96485 C/mol), d_{metal} density of the metal (for Al d_{Me} = 2700 kg/m^3). Therefore we have to determine corrosion current. This is calculated by

$$I_{corr} = \frac{1}{2.3}.\frac{b_a.|b_c|}{b_a + |b_c|}\frac{\Delta I}{\Delta E} \qquad 2.8$$

which is Stern-Geary relation. b_a and b_c are inverse of the slopes of the Tafel plot, anodic and cathodic branches respectively. $\Delta I / \Delta E$ is called the polarization conductance, K_{corr} and its inverse polarization resistance, R_p. One of the methods for determining R_p in the laboratory is impedance experiment.

$$R_p = Z_{\omega \to 0} - Z_{\omega \to \infty} \qquad 2.9$$

Measurements of the series resistance at the high frequency limit normally presents few problems. On the other hand, in low frequency region special precautions must be adopted to obtain reliable data [5].

2.2. CONDUCTING POLYMERS

2.2.1. Background of Conducting Polymers

We are used to polymers –that is, plastics- being somehow opposite of metals. They were thought of as insulators and any electrical conduction in polymers was generally regarded as an undesirable phenomenon. The residual conductivity in common polymers can mostly be assigned to loosely bound protons. In the last decades an opposite trend has started in as much as examinations directed to the utilization of ionic conductivity of polymeric systems. Also in 1977 Shirakawa, MacDiarmid and Heeger somewhat surprisingly discovered that oxidation with chlorine, bromine or iodine vapor, made polyacetylene films 10^9 times more conductive than they were originally [6]. Treatment with halogen was called "doping" by analogy with the doping of semiconductors. It is well established that the electrical conduction properties of elemental semiconductors such as Si may rigorously controlled by the addition of very small quantities of foreign atoms into the host semiconductor lattice. The host semiconductor may be n type or p type depending on the nature of the added dopant atoms, that is, whether the latter has an excess of deficit electrons. New dopant energy levels are introduced into the band gap and conduction is facilitated. The conductivity level attained depends strongly on the concentration of donor or acceptor species incorporated. Excess conduction electrons or holes are generated n the material as a result of doping and so conductivity is enhanced. A similar terminology has been applied to conjugated polymers. These materials may also be "doped " and indeed the conductivity level obtained will depend on the doping level. However the doping mechanism differs considerably from observed for elemental semiconductors. First, the doping levels attained in conjugated polymers are significant (doping levels can be as large as %10 mol). Second, one has charge transfer between the incorporated dopant atom and the polymer chain [7]. This class polymers possessing high electronic conductivity (electronically conducting polymers or plastic metals) are still in the foreground of research activity. There are at least two major reasons for this intense interest. First is the intellectual curiosity of scientists that focuses on understanding the behavior of these systems, in particular on the mechanism of charge transfer and charge transport processes occurring in the course of redox reactions of conducting polymeric materials. Second is the wide range of promising applications in the field of energy storage, electrocatalysis, organic electrochemistry, bioelectrochemistry, photoelectrochemistry, electroanalysis, sensors, electrochromic displays, microsystem technologies, electronic devices, microwave screening and corrosion protection etc. [8]. These novel materials with interesting and unanticipated properties have attracted the whole scientific community including polymer and

synthetic chemists, material scientists, organic chemists, analytical chemists, as well as theoretical and experimental physicists.

The fundamental nature of charge propagation on the whole is understood, i.e. the transport of electrons can be assumes to occur via an electron exchange reaction (electron hopping) between neighboring redox sites in redox polymers (Fig.2.2.a) and by the motion of delocalized electrons through conjugated systems in the case of so-called intrinsically conducting polymers (ICPs) (Fig.2.2.b) Main difference of ICPs is electronic conduction of the backbone itself.

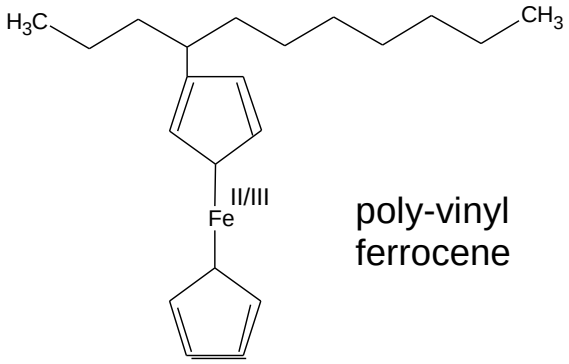


Figure 2.2.a. Typical redox electroactive polymer

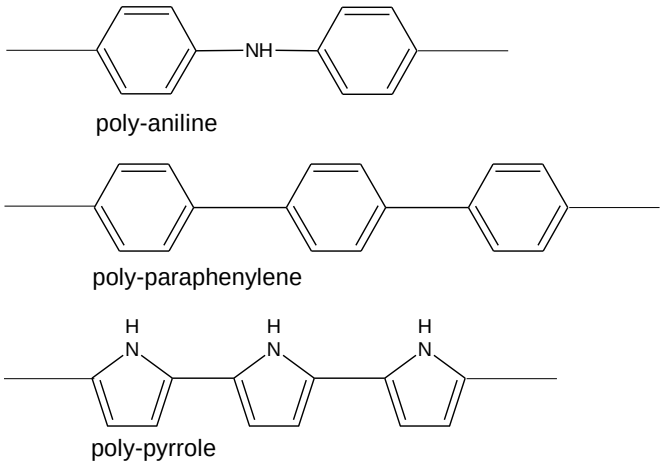


Figure 2.2.b. Some examples of intrinsically conducting polymers (ICPs)

In this study we will focus on ICPs, because in corrosion protection applications mainly they are used. Most of the reported studies concern PPy and polyaniline (PANI) owing their long term stability and efficiency. Both theoretical calculations and experimental studies indicate that the precise nature of charge carriers in conjugated polymer materials depends on the type of polymer.

2.2.2. Synthesis and Structure

Polymers can be prepared by both methods using chemical and electrochemical methods of polymerization. The majority of redox polymers have been synthesized by chemical polymerization. From the applied point of view the electrochemical polymerization of cheap simple aromatic benzoid or nonbenzoid (mostly amines, e.g. aniline, 0-phenylenediamine), and heterocyclic compounds (e.g. pyrroles, thiophenes, azines) is of utmost interest [8]. The reaction is usually oxidative polymerization. Owing to chemical diversity of the compounds studied a general scheme cannot be given. However, in the case of heterocyclic compounds such as pyrrole we studied in his work, it has been proved that the first step is the formation of cation radicals. The further fate of these highly reactive species depends on the experimental conditions (composition of the solution, temperature, potential or rate of the potential change, galvanostatic current density, material of the electrode, state of the electrode surface etc). In favorable case the next step is a dimerization reaction and then stepwise chain growth proceeds via association of radical ions or that of a cation radical with a neutral monomer (Fig 2.3) [9]. Even there might be parallel dimerization reactions leading to different products or to the polymer of disordered structure. The inactive ions present in the solution may play a pivotal role in the stabilization of the radical ions, they known as buffers.

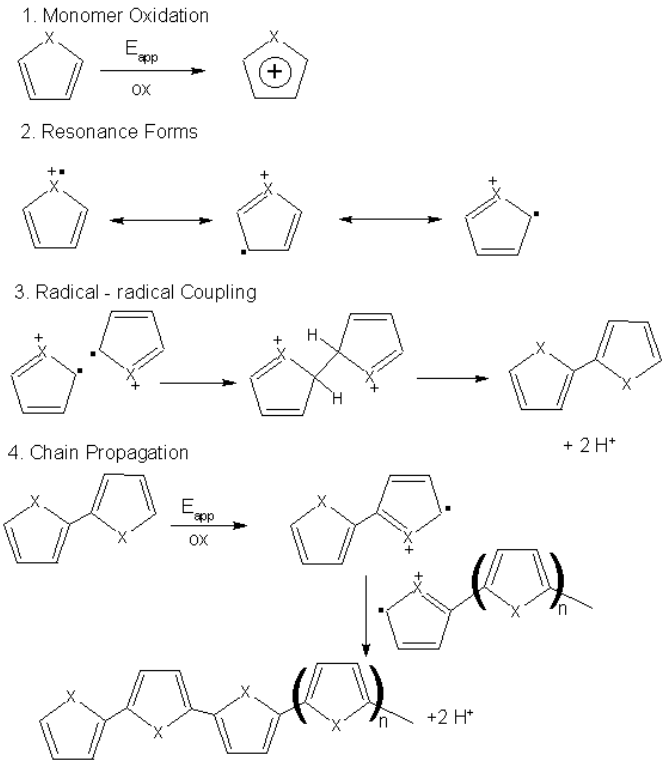


Figure 2.3. More detailed look at PPy formation

The polymers are obtained in an oxidized, high conductivity state containing incorporated counterions from the solution used in preparation procedure. It is easy to change the oxidation state of the polymer electrochemically, e.g. by potential cycling between oxidized, conducting and the neutral, insulating state. These oxidation-reduction reactions can be classified into three general types, based on the nature of the doping process:

a. Type 1: protonic/electronic doping involving both proton and anion incorporation into polymer (e.g. polyaniline, Fig 2.4)

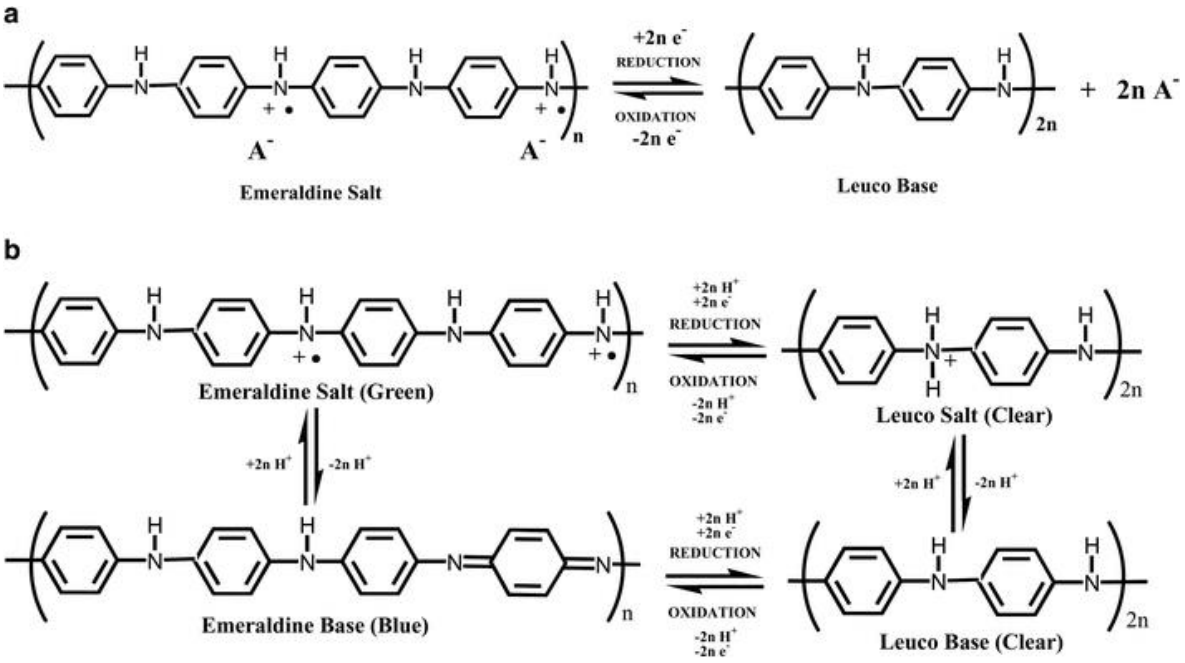


Figure 2.4 a. Type 1 ICP, polyaniline redox scheme showing anion A^- expulsion upon reduction

b. Polyaniline square scheme showing the proton and electron transfers (the anions associated with the salt forms are omitted for clarity). Fully oxidized form is not shown

b. Type 2: electronic doping with anion incorporation (e.g. polypyrrole or polythiophene, Fig 2.5)

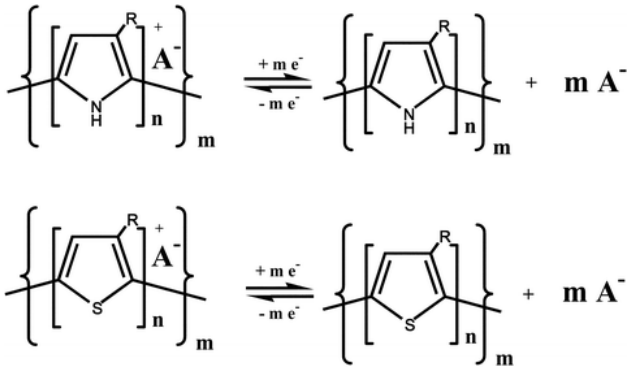


Figure 2.5 Type 2 ICP polypyrrole (top) and polythiophene (bottom) redox scheme showing anion (A^-) expulsion upon reduction. Typically n=2,4 symbolizing a positive charge for every 2-4 monomer units.

c. Type 3: electronic doping with cation expulsion, either form a covalently attached acid group (also called self doped, e.g. sulfonated polyaniline, (Fig2.6) or from a sufficiently large, physically entrapped, immobile acid (or salt, e.g. a polyelectrolyte).

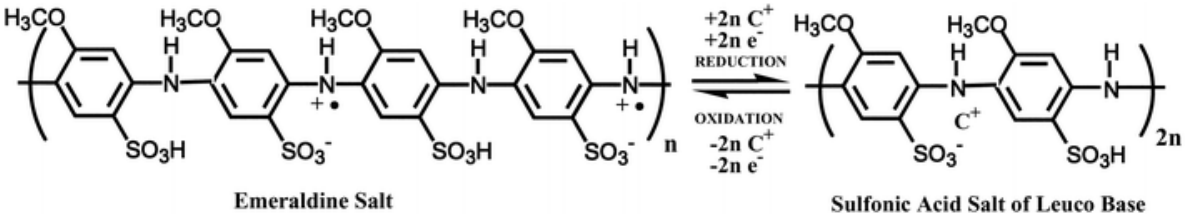


Figure 2.6. Type 3 ICP a sulfonated (or self-doped) polymaniline redox scheme showing cation (C^+) incorporation upon reduction

All three types of polymers have been and continue to be investigated for use in corrosion control coatings, either directly as a primer coating or surface treatment, or as a component blended with more conventional coatings.

ICPs are redox active materials, with equilibrium potentials that are positive relative to those of iron and aluminum, as is potential of chromate (Table2.1) [10]. The potentials suggest that mechanism is likely to involve anodic protection. However, other factors may also be important such as metal complexition, perhaps with suitable interface stabilization and counter ion release, where the counterion might be selected for its known corrosion inhibition.

Table 2.1. Comprasion of reduction potentials of some substrates

Redox Couple	Reduction Potential (vs.SHE at pH7)
Mg/Mg^{2+}	-2.36
Al/Al_2O_3	-1.96
Zn/Zn^{2+}	-0.76
Fe/Fe^{2+}	-0.62
H_2/H_2O	-0.41
H_2O/O_2	+0.82
CrO_4^{2-}/Cr_2O_3	+0.42
Polypyrrole	-0.1 to +0.3[a]
Polyaniline	+0.4 to +1.0 [a]
Polythiophene	+0.8 to +1.2[a]

[a] For the ICPs an approximate range of electroactivity is provided, the actual resuction potentials depending on the dopant and doping level, the electrolyte and other experimental variables. These potential ranges can be further modified by placing appopriate substituents on the polymer ring system.

2.3. PASSIVATION OF Al BY CONDUCTING POLYPYRROLE

2.3.1. Overview

While protecting the metals against corrosion by surface modification with conducting polymer based films the concept is to stabilize stationary potential within passive range by exploring the ability of conducting polymer forming robust films to accumulate sufficient amount of charge that allows to hold constant and positive enough potential that leading to the stabilization of a passive layer on passivating metals. To achieve this goal charge stored in the oxidized polymer must be capable of compensating the anodic current originating form dissolution of passivated metal. Also these partially oxidized polymers are positively charged and they show anion exchange properties therefore thin films of ICPs protect metal by blocking the access of aggressive (e.g. Cl) ions, and addition to this they even tend to preconcentrate anions. Furthermore polymer hosts mobile protons, which are necessary to support reactions, oxygen reduction and formation of passive oxides.

2.3.2. Properties of Pyrrole

Pyrrole first discovered in 1834 by Runge in coal tar. Later on Anderson also discovered it in bone oil the product obtained by distilling bone meal. If pine splint is moistened with HCl it turns red when exposed to the vapor of Py. This test reaction was responsible for giving pyrrole its name. (Greek: pyrros = fiery red)

In an older form of nomenclature, now only seldom used, positions 2 and 5 were called α and α' positions and position 3 and 4 were called β and β' positions. When the hydrogen atom on the nitrogen atom is replaced by subsistent, this is named as *N*-substituted product (Fig2.7).

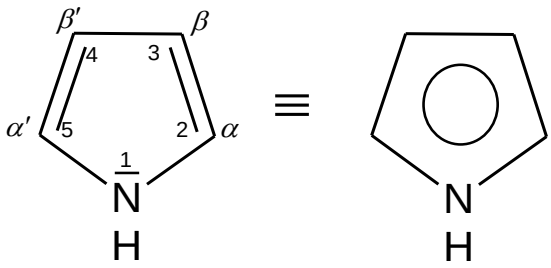


Fig.2.7. Nomenclature of pyrrole

- Preparation of Py

I) Py can be obtained by heating *but-2-yn-1,4-diol* with *ammonia* under pressure

II) Industrial Py is prepared from *furan* and *ammonia*

III) Paal-Knorr Synthesis. 2,5-Dialkyl- and 2,%-diaryl-pyrroles can be prepared by heating 1,4-diketones with ammonia

- Properties of Py

Freshly distilled Py is colorless liquid, b.p. 131°C. It turns brown in the air and gradually resinifies. It is only slightly soluble water but is totally miscible with ethanol or ether.

Py can be described in terms of the following limiting structures [12] (Fig 2.8):

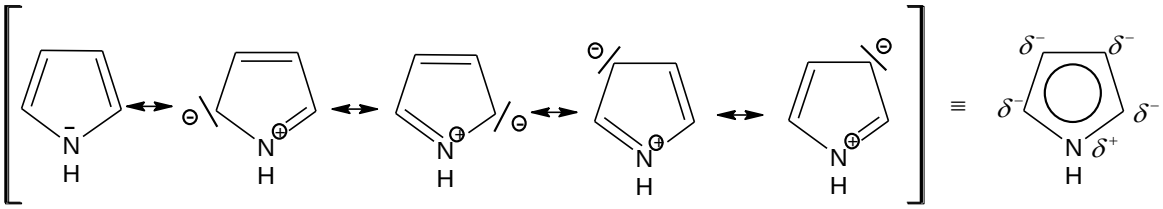


Figure 2.8. Resonance structures of pyrrole

2.3.3. Formation and Character of PPy Film

As mentioned above aluminum electrodes easily oxidized to form Al^{3+} species giving nonconducting dielectric Al_2O_3 film on the electrode. The Al_2O_3 film inhibits electron transfer and thus inhibits the electrochemical formation of PPy on it. A few authors have reported successful results. [12-15]. Therefore, the PPy and the thin Al_2O_3 films have not been well characterized. (Fig. 2.9) shows a brief model for the

electron and mass transports during the simultaneous electrochemical formation of Al_2O_3/PPy films on Al surface. [16]

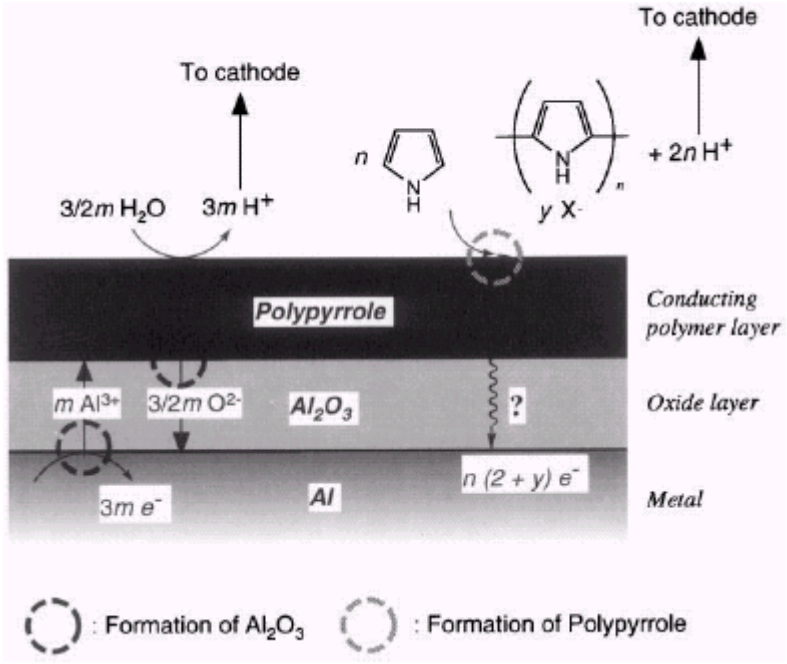


Figure 2.9. A schematic model for an electrochemical simultaneous formation of the Al_2O_3/PPy layers on Al electrode

The formation of Al_2O_3 proceeds at two interfaces, at the aluminum/Al_2O_3 and at the Al_2O_3/Ppy. Al^{3+} species continuously generated at metal/oxide interface. Then they migrate through growing Al_2O_3 layer and toward the solution under high electric field while oxide ions O^{2-} migrate toward the aluminum electrode. At the interface of Al_2O_3/Ppy the Al^{3+} encounters water species to form Al_2O_3 film. In the anodization process of Al electrode electrolyte anion plays a key role in determining the type of oxide film and its current efficiency.

In order to get thick oxide film of Al_2O_3 mainly there are two approaches. First is using surfactant electrolytes [14, 16]. Here electrolyte plays three important roles: (1) as supporting electrolytes for forming Al_2O_3 film, (2) dopants incorporated in the electropolymerized PPy film and most importantly (3) micelle assemblies at the electrode interface to enable the PPy formation simultaneously with the formation of the insulating oxide under layer film. Second method consists of pretreatment of the

Al surface [12-13] such as diamond polish or galvanic activation of the surface. In galvanic activation by-pass the barrier layer by formation of pits, via very high current densities in acidic media, with overoxidized PPy islands in it. Overoxidized PPy have inferior conducting and mechanical properties [9] but they let the PPy film to formation.

The mechanisms by which ICPs like PPy function as corrosion control agents are still under investigation, but a few general concepts are beginning to emerge.

First, the oxidized form of an ICP does not make good barrier coating since the rather high ionic content of the content of the polymer permits easy ingress of water and other ions. Such coating without a topcoat do not last very long when subjected to immersion of salt spray, It is not altogether clear whether these observations are a result of the better barrier properties of this form or are due to other properties of the polymer such as its oxidation state, ability to form complexes with metal ions. Etc.

Second, as noted above the redox state of the ICP is certainly an important factor. Because of the corrosion control is attributed to the ability of the ICP to maintain the metal in a passive potential regime, a result of the oxidative power of the ICP and also of the galvanic coupling between the metal and the polymer, which in turn is possible because both the metal and ICP are electronic conductors. This phenomenon would explain the ability of the ICP to protect exposed metal in a defect. One would not expect significant galvanic coupling in this cases but the other hand, partial doping of the polymer through interactions with metal and/or the electrolyte may lead sufficient conductivity.

Third, the electronic conductivity of these polymer films probably plays an important role, not only galvanic coupling mentioned above, but also for providing an interface at which the cathodic reaction can take place. Additionally, the cathodic reaction such as oxygen reduction would be removed from metal interface, occurring instead at the ICP surface.

Finally there is the issue of adhesion of ICP to the active metal surface. An advantage of incorporating ICPs into a binder such as epoxy or polyurethane is the good adhesion that such binders provide and there are commercial products in this way such

as CORRPASIV that consists PAni (www.ormecon.de). But with this approach typically less ICP contacts with the metal surface perhaps a reduction in corrosion protection. Adhesion of ICPs coated with direct electropolymerization still needs to be improved and it is subject of researches.

2.4. Polarization Curves – Tafel Plots

When a metal is not in equilibrium with a solution of its ions the electrode potential differs from the equilibrium potential by an amount known as the polarization. Other terms having equivalent meaning are overvoltage and overpotential. Polarization is an extremely important corrosion parameter because it allows useful statements to be made about rates of corrosion processes.

In 1905, Julius Tafel found for a cathodic polarized electrode that the current density i correlates logarithmic with the potential applied according to;

$$E = a \pm b \log|i| \qquad 2.10$$

where E is the potential measured with respect to selected reference electrode and with *a* and *b* constants. The Tafel equation has been confirmed experimentally for a wide variety of individual anodic and cathodic reactions. Constant a and b can be predicted theoretically for many reactions [16].

For a simple electrode process with only one anodic and cathodic partial reaction, i.e. charge transfer controlled metal dissolution and metal deposition, the Tafel equation is the logarithmic form of the Butler-Volmer equation that correlates the current to applied potential, for large over potentials. The B.-V. Equation for charge transfer controlled redox reaction can be expressed as

$$i = i^{+} + i^{-} = |i_0| . \left\{ e^{\frac{\alpha z F}{RT}(E-E_0)} - e^{\frac{-(1-\alpha) z F}{RT}(E-E_0)} \right\} \qquad 2.11$$

where i is current density, $|i_0|$ is exchange current density, α is symmetry factor, E is applied electrode potential and E_0 is equilibrium potential. Using Tafel's relationship (Eq. 2.11) it is possible to determine i_0 by measuring the current density – potential curve, and extrapolating to E_0 on a semilogarithmic plot. Experimentally this graph as

in (Fig. 2.10). The anodic and cathodic Tafel constants b_a and b_c in this case would be:

$$b_a = \frac{2.3RT}{\alpha zF} \quad \text{and} \quad b_c = \frac{2.3RT}{(1-\alpha)zF} \qquad 2.12a \quad 2.12b$$

which are can be obtained from slope of the extrapolated tafel lines. They are used in (Eq. 2.8)

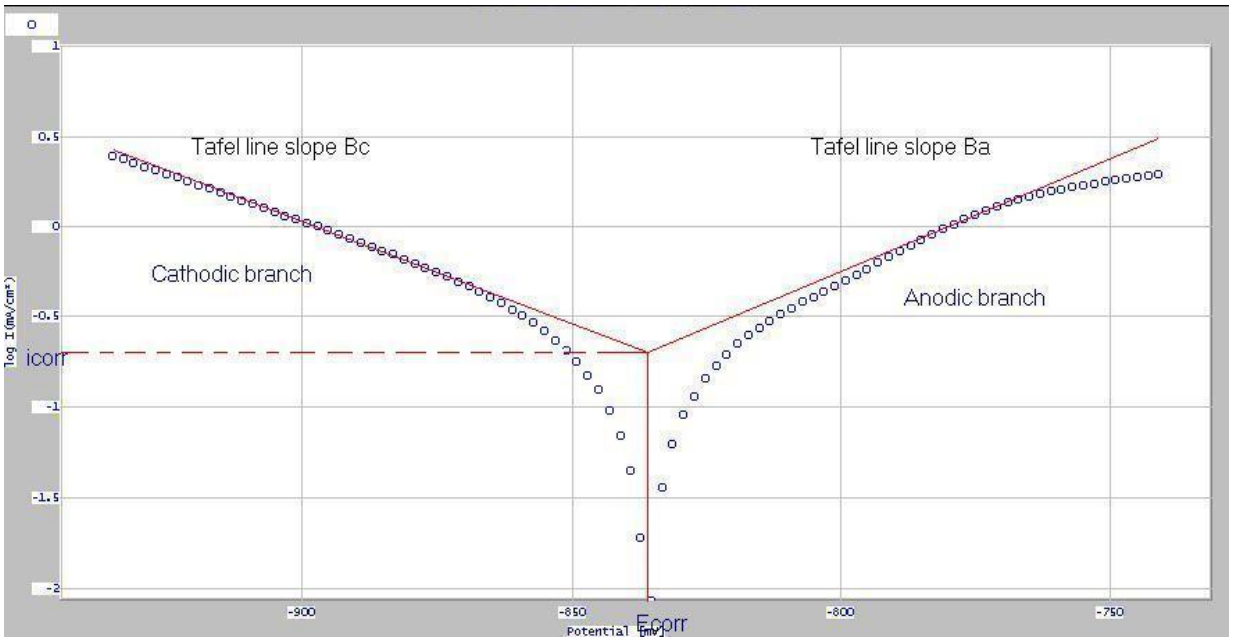


Figure 2.10 Tafel plot and extrapolation of the E_0 and i_0 with sample Inox Steel 10/18 in 1M H_2SO_4 [18]

If there are more than two partial charge transfer reactions involved –as it is always the case for a corroding system- the simple Tafel relation will still be valid since the partial currents are algebraically additive.

2.5 Electrochemical Impedance Spectroscopy

2.5.1 EIS Fundamentals

In essence what one does is to examine the sinusoidal voltage response of an electrochemical system to a small-amplitude sinusoidal current perturbation. Let the perturbation have the form

$$\nabla I = I_m \sin \omega t \qquad 2.13$$

where I_m denotes the amplitude of the perturbation. Then the response will have the form

$$\nabla V = V_m \sin(\omega t - \phi) = V_m (\cos\phi \sin\omega t - \sin\phi \cos\omega t) \qquad 2.14$$

where ϕ denotes the phase angle. The impedance is then calculated for specific frequency ω using the relation

$$Z(\omega) = \nabla V(\omega) \big/ \nabla I(\omega) \qquad 2.15$$

The relationship between ΔV and ΔI is completely determined by the ratio of the amplitudes V_m / I_m and the phase shift ϕ between current and voltage. This procedure is repeated over a very large frequency range, ideally from 100 kHz to 0.1 mHz. The result is that one obtains an impedance profile or spectrum $Z(\omega)$ as a function of frequency ω.

The response of any linear system to a perturbation of arbitrary form may be described by a transfer function

$$H(s) = \frac{\bar{V}(s)}{\bar{I}(s)} \qquad 2.16$$

where s is the Laplace frequency and $\bar{V}(s)$ and $\bar{I}(s)$ are the Laplace transforms of time dependent voltage and current, respectively. In term of steady state sinusoidal frequency domain, the transfer function becomes

$$H(j\omega) = \frac{F\{V(t)\}}{F\{I(t)\}} = \frac{V(j\omega)}{I(j\omega)} \qquad 2.17$$

where F signifies the Fourier transform and $V(j\omega)$ and $I(j\omega)$ are the sinusoidal voltage and current. That is the indirect way of applying Ohm's law to time dependent systems. But this method can applicable if only system's behavior is linear so that it can be expressed by system of linear differential equations. Because all linear differential equations can be transformed in to Laplace-domain it is useful to solve voltage/current dependences in Laplace domain and then into required time domain equations by reverse Laplace transformation. Solving in Laplace domain is relatively easy because these dependencies exactly look like Ohm's law of elements including time dependent ones, such as capacitors and inductances. Provided that system is linear, causality is obeyed, and the interface is stable over the time of sampling, transfer function may be identified as impedance, $Z(j\omega)$. Because they are vector quantities $H(j\omega)$ and $Z(j\omega)$ are complex numbers containing both magnitude and phase information.

Since the impedance is a complex number, it is commonly written as,

$$Z(j\omega) = Z' - jZ'' \tag{2.18}$$

where $j = \sqrt{-1}$ and Z' and Z'' are frequency dependent real numbers, which are related to the magnitude of the impedance and phase by

$$|Z(j\omega)| = \sqrt{Z'^2 + Z''^2} \tag{2.19}$$

$$\tan\phi = -\frac{Z''}{Z'} \tag{2.20}$$

The parameter ϕ is the phase angle. Alternatively the complex impedance may be expressed as

$$Z(j\omega) = |Z|e^{j\phi} \tag{2.21}$$

where $|Z|$ is the impedance modulus. The equivalent mathematical forms of the complex impedance given by (Eq. 2.19) and (Eq. 2.21) lead directly to the two common methods for displaying impedance data, as $-Z''$ versus Z' (Nyquist or complex plane) and as $\log|Z|$ and ϕ versus $\log\omega$ (Bode plane). Each offers specific advantages. The complex plane is more useful for mechanistic analysis, because of the number of relaxations and their mechanistic implications are often more apparent. On the other hand, the Bode plane employs frequency directly as the independent variable, so that more precise comparison between experimental and calculated impedance spectra can be made. One displaying style is proposed by MacDonald is

three-dimensional plot consisting of compilation of Bode and Nyquist representations. It is sometimes useful to display data in the form of admittance *Y* that is defined as

$$Y \equiv Z^{-1} \equiv Y' + jY'' \qquad 2.22$$

After the general shape of the impedance spectrum is obtained then it may be modeled in terms of an equivalent circuit consisting for example, of resistance and capacitance circuit elements combined in definite ways (series of parallel combinations) that can be relatively simple or complex combinations, depending on the degree of complexity of the system under study. This correspondence between an impedance spectrum and an equivalent circuit is well established in basic physics. These circuit elements reflect various physical features of the real electrochemical system under study. A flow diagram of a general characterization procedure using EIS is presented in (Fig. 2.11).

The main difficulty is to devise an unambiguous equivalent circuit representation for a specific system. This can pose problems because of the fact that the system may be adequately described by a number of different equivalent circuits. This is also known weakness of the method. Because one could propose different equivalent circuits therefore different reaction mechanisms are proposed, this brings to method considerable subjectivity.

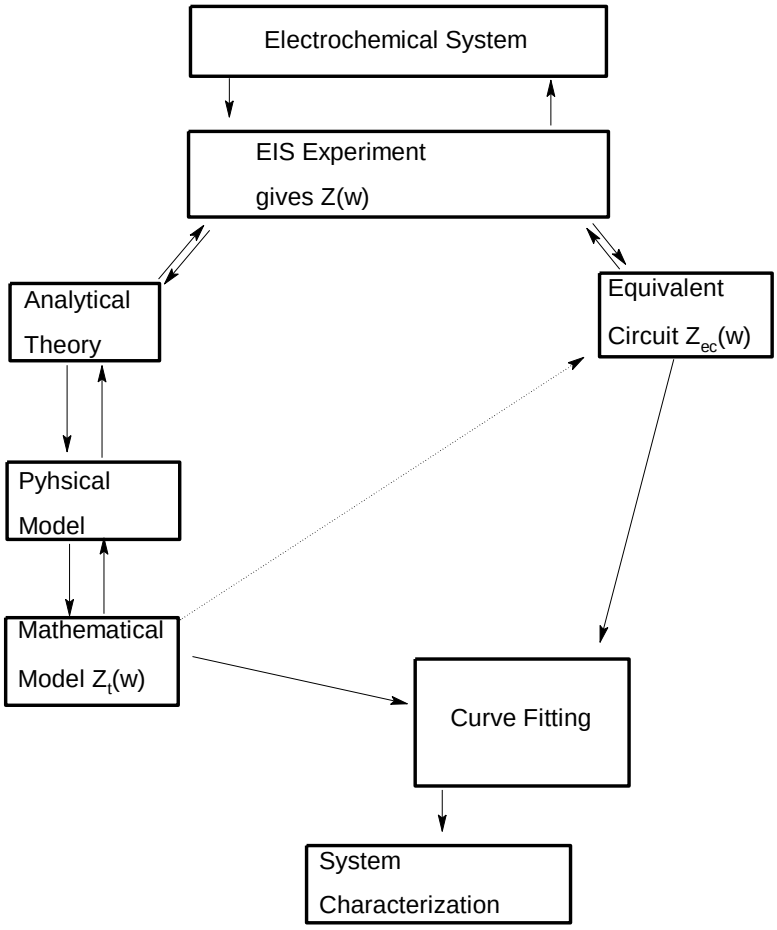


Figure 2.11. Flow diagram for the measurement and characterization of a material electrode system

2.5.2 Equivalent Circuits

Equivalent circuit is mainly combination of resistances and capacitances (inductances for very high frequencies and special cases). This circuit should contain at very least components to represent:

- The double layer; a pure capacitor of capacity C_d
- The impedance of faradic processes Z_f
- The uncompensated resistance R_Ω which is usually the solution resistance between working and reference electrodes

The combination of these elements is shown in (Fig.12a) with Z_f and C_d in parallel. The impedance Z_f can be subdivided in two equivalent ways as (Fig.12b). First one is to take it as a series resistance-capacitance combination comprising the series resistance R_s and pseudocapacity C_s . Second alternative is to separate a pure

resistance R_{ct} charge transfer resistance and another general impedance Warburg impedance Z_w which represents a kind of resistance to mass transfer. This circuit commonly referred as Randles circuit. In contrast to R_Ω and C_d which are nearly ideal circuit elements the components of faradic impedance are not, because they change with frequency.

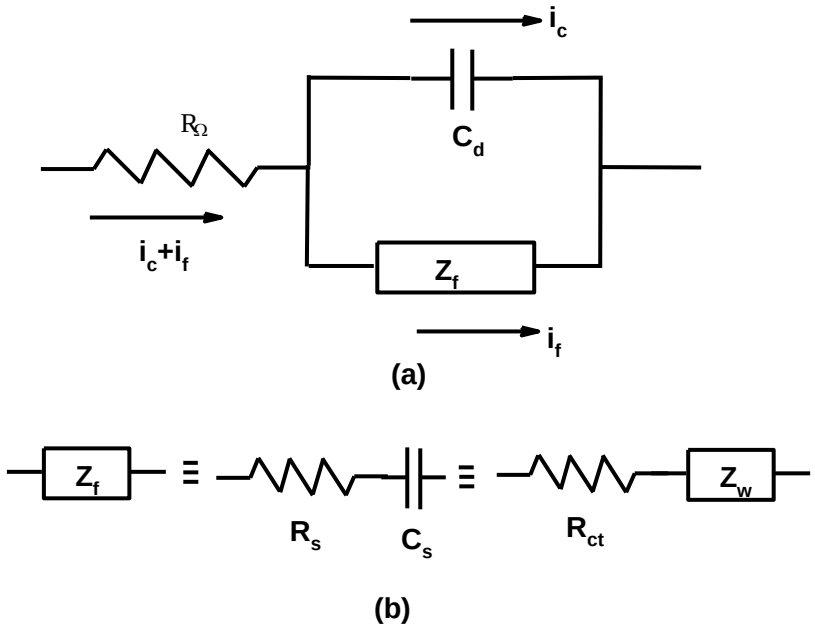


Figure 2.12 (a) Equivalent electrical circuit of an electrochemical cell for simple electrode process. (b) Subdivisions of Z_f into R_s and C_s or into R_{ct} and Z_w

It can be shown for the Randless circuit for simple charge transfer reaction such as $M^{n+}(aq) + ne^- \longrightarrow M$ on separating in phase and out of phase components of the impedance, that [18]

$$Z' = R_\Omega + \frac{R_{ct} + \sigma\omega^{-1/2}}{(\sigma\omega^{1/2}C_d + 1) + \omega^2 C_d{}^2 (R_{ct} + \sigma\omega^{-1/2})^2} \qquad 2.24$$

$$-Z'' = \frac{\omega C_d (R_{ct} + \sigma\omega^{-1/2})^2 + \sigma^2 C_d + \sigma\omega^{-1/2}}{(\sigma\omega^{1/2}C_d + 1)^2 + \omega^2 C_d{}^2 (R_{ct} + \sigma\omega^{-1/2})^2} \qquad 2.25$$

where ω is angular frequency and σ is defined as

$$\sigma = \frac{RT}{n^2 F^2 A\sqrt{2}}\left(\frac{1}{D_o^{1/2}[O]_\infty} + \frac{1}{D_R^{1/2}[R]_\infty}\right) \qquad 2.26$$

where R is gas constant, F is Faraday constant, A is area of electrode, D_O and D_R are diffusion coefficients of oxidized and reduced species respectively, $[O]_\infty$ and $[R]_\infty$ are bulk concentrations of this species.

When one considers the limiting forms of these equations:

- Low frequency limit is straight line of unit slope, which extrapolated to the real axis gives an intercept of $\left(R_\Omega + R_{ct} + 2\sigma^2 C_d\right)$. The line corresponds to a reaction controlled solely by diffusion and the impedance is the Warburg impedance, the phase angle being $\pi/4$ as seen in (Fig. 2.13).

$\omega \to 0$

$$Z' = R_\Omega + R_{ct} + \sigma\omega^{-1/2} \qquad 2.27$$

$$Z'' = -\sigma\omega^{-1/2} - 2\sigma^2 C_d$$

- At the high frequency limit the control is purely kinetic, and $R_{ct} >> Z_w$. The electrical analogy is a resistance and capacitance in parallel combination.

$\omega \to \infty$

$$Z' = R_\Omega + \frac{R_{ct}}{1+\omega^2 C_d{}^2 R_{ct}{}^2} \qquad 2.28$$

$$Z'' = -\frac{\omega C_d R_{ct}{}^2}{1+\omega^2 C_d{}^2 R_{ct}{}^2}$$

and by simplification

$$\left(Z' - 1 + R_\Omega - \frac{R_{ct}}{2}\right)^2 + \left(Z''\right) = \left(\frac{R_{ct}}{2}\right)^2 \qquad 2.29$$

that is the equation a circle with radius $R_{ct}/2$ as in (Fig. 2.13).

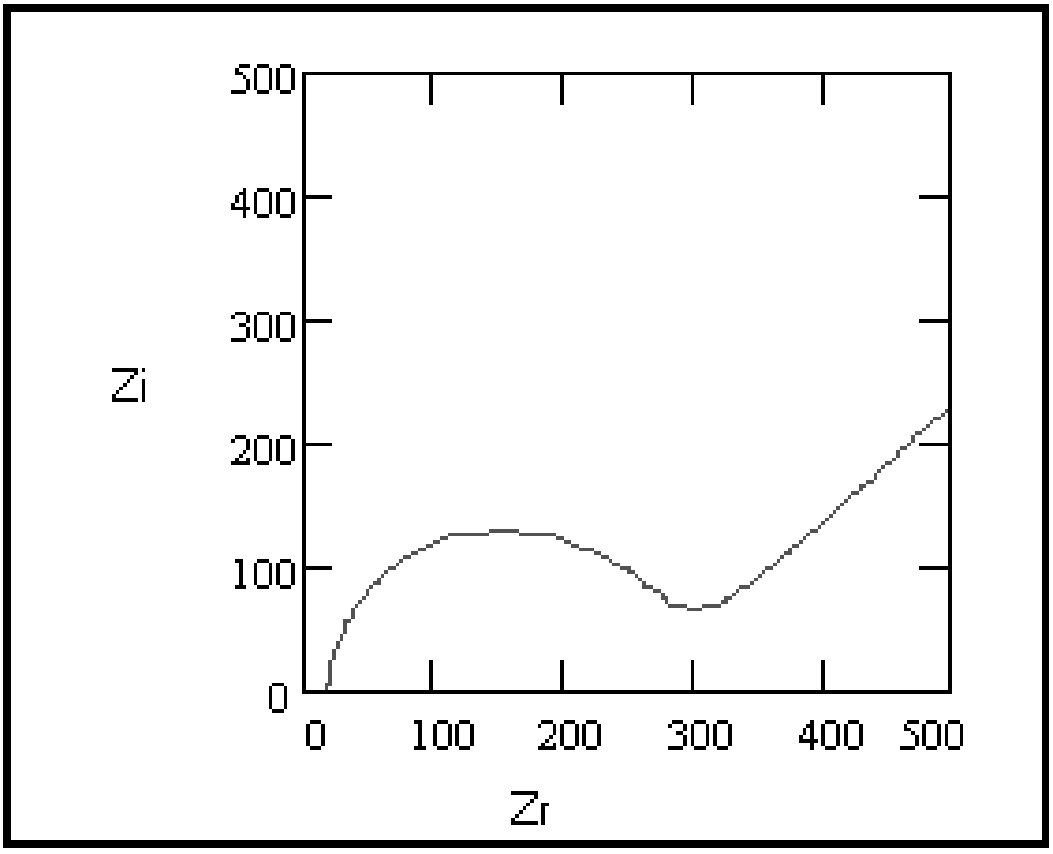


Figure 2.13. Plot of impedance in the complex plane of a simple electrochemical system $O+ne^- \rightarrow R$

3. EXPERIMENTAL WORK

3.1. Materials and Chemicals

Aluminum Alloy 6063 (thickness 0.5 mm) was supplied by Fen-İş Company and its chemical composition according to TSE 412 [20].

Table 3.1.1. Chemical composition of Al 6063

Si:	0.20-0.60 %	**Cr:**	0.10 % max.
Mg:	0.45-0.90 %	**Cu:**	0.10 % max.
Fe	0.35 % max.	**Mn:**	0.10 % max.
Ti:	0.10 % max.		
Misc:	Each 0.05%, total 0.15% max		

Chromate treated Al 6063 (1cmx1cmx5cm) was also supplied by Fen-İş Company

Water was twice distilled Millipore quality pure.

Pyrrole was used as monomer was a product of Merck and used directly.

1- MethylPyrrole was used as monomer was a product of Acros and used directly.

Oxalic acid was a product of Merck and solved in water.

PotassiumChlorur was a product of Merck.

Two-component epoxy used as seal was a product of Devcon

Acetone (technical grade) used in degreasing of Al6063

Reference electrodes Ag/AgCl was a product of Radiometer Analytical Company

Platinum meshes used as counter electrode in coating experiments

Indium mesh used as counter electrode in characterization experiments

3.2. Equipments

3.2.1. Electrochemical Cell

Basic three-electrode, general purpose electrochemical cell was used; its body was double jacketed in order to control the reaction temperature.

3.2.2. Electrochemical Measurements

Radiometer Analytical Comp. Voltalab 40 system that consists PGZ 301 potentiostat with VoltaMaster4 software was used.

3.2.3. SEM Measurements

SEM measurements have been made wit Jeol JSM 5600 model scanning electron microscope that have working ranges between 0.01 – 30 kV and zoom ranges between 35-300.000.

3.3. Galvanostatic Electrochemical Deposition of Pyrrole on Al 6063

Aluminum 6063 sheets were employed as strips, partially covered with self-adhering PTFE tape; they had accessible free area of 4 cm^2. After aluminum 6063 degreased with acetone in ultrasonic bath 15 minutes [21], according to Beck's method [11] to get smooth and adhesive coatings before coating process there must be a pretreatment step which known as galvanostatic activation (GA). This step was made in 0.1 M HNO_3 / 0.1 M Py at 24 $mA.cm^{-2}$ for 2 minutes under nitrogen environment at 20 ^oC. Thereafter Al sheet was thoroughly rinsed with water. Galvanostatic electrodepositions were run at 0.5 and 1 $mA.cm^{-2}$ in nonstirred electrolytes.

3.4. Electrochemical Measurements

All electrochemical measurement experiments were done in room temperature, in 0.1M KCl solution was used as the electrolyte solution and aerated environment. Al sheets partially sealed with epoxy resin.

Polarization curves were taken after 15 minutes OCP measurements in order to stabilize OCP and let the system reach the equilibrium. The potential range from –400mV to 600mV versus the OCP at a scan rate of 2 mV/s. Tafel plots were drawn by extrapolation of polarization curves with VoltaMaster software.

Impedance spectroscopy measurements were performed in the frequency range $0.05\text{-}4.10^4$ Hz. Excitation signal amplitude was 0.1 mA without any DC current. Results were examined with LEVM software which written by J. R. Macdonald.

Every experiment was repeated at least 3 times with different Al strips and electrolytes to ensure the reproducibility.

3.5. SEM Measurements

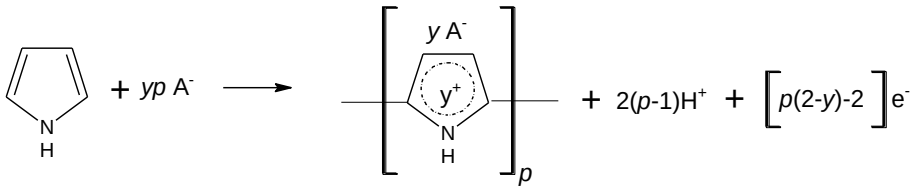
Mainly two oxalic acid doped PPy coated samples examined with SEM analysis. One was never immersed in any solution and other one was immersed in 0.1 KCl solution for 65 hours. They were examined at zoom ranges 200, 1500 and 3000. Experiments were made with 15 kV working voltage.

4. RESULTS AND DISCUSSION

4.1. Galvanostatically Electrochemical Deposition of Pyrrole on Al 6063

4.1.1. Definition of nominal layer thickness, d_n

PPy is formed by anodic α,α-coupling of pyrrole rings. At the potential of the electropolymerization, every segment of conjugated backbone, containing there of four monomer units, is further oxidized to yield the polymeric radical cation. The overall process can be written as



4.1

where p is the degree of polymerization, and y a stochiometric factor. A^- is the anion, which is inserted for charge compensation. From this model theoretical electrochemical equivalent $m_{e,th}$ can be derived as for high degrees of polymerization

$$m_{e,th} = \frac{M}{zF} = \frac{M_M + yM_A}{(2+y)F} \qquad 4.2$$

where M_M is the molecular weight of the monomer unit in the polymer ($M_M = M_{py} - 2 = 65$) and M_A is the molecular weight of the anion. y is the above mentioned degree of insertion. A nominal thickness d_n of the layer follows (Eq. 4.2) using Faraday law [22]:

$$d_n = \frac{Q_A}{\rho}\frac{M_M + yM_A}{(2+y)F} = \frac{Q_A m_e}{\rho} \qquad 4.3$$

where ρ is the density of polypyrrole, which was found to be 1.50 for generally doped polypyrrole[23]. Q_A is the area specific overall charge for electropolymerization.

4.1.2. Coating of Al 6063

Several experiments was done with two different dopants and two monomers; oxalic acid and paratoluenesulphonic acid (pTS) as dopants and pyrrole (Py) and 1-Methyl Pyrrole(MPy) as monomers. However a homogenous and adhesive layer was obtained only with oxalic acid. In the case of pTS coating had pits inside and was heterogeneous so it was inadequate to use as corrosion resistant coating. Typical galvanostatic electrodeposition curves shown in (Fig 4.1)

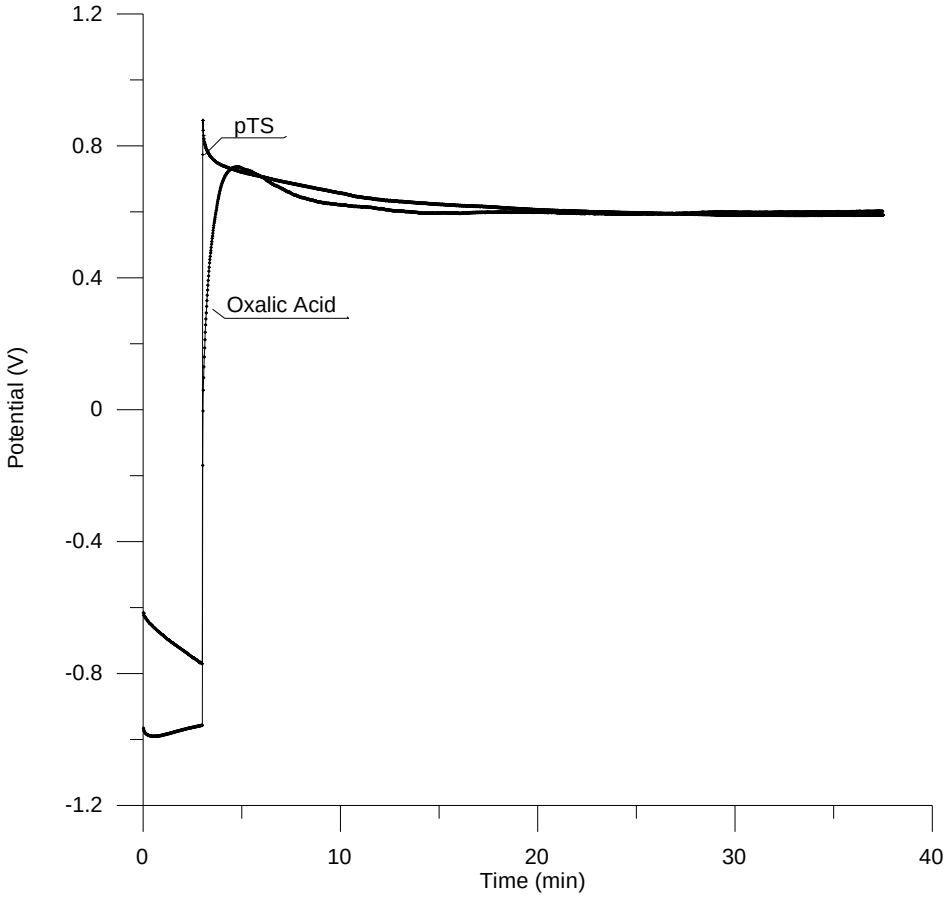


Figure 4.1. Potential – Time Curves for the galvanostatic electrodeposition of PPy (d_n = 3 μm) from aqueous electrodes at Al 6063 with different dopants; 0.1 M Oxalic Acid and 0.1 M pTS, with current density 0.5 mA cm^{-2}

Electrochemical conditions and resulting coatings were presented in (Table 4.1)

Table 4.1. Galvanostatic Electrodeposition Conditions and Results on Al 6063

Dopant	Monomer	Current Density (mA)	Time (min)	Coating
$C_2H_2O_4$	Py	0.5	35	+
$C_2H_2O_4$	Py	1	21	+
PTS	Py	0.5	35	-
PTS	Py	1	25	-
$C_2H_2O_4$	1MPy	2	15	-
$C_2H_2O_4$	1MPy	0.5 + 2	25 + 24	+

Interesting point here was 1MPy coating, they needed two currents steps to achieve good coating and their potential – time responses as shown below (Fig. 4.2).

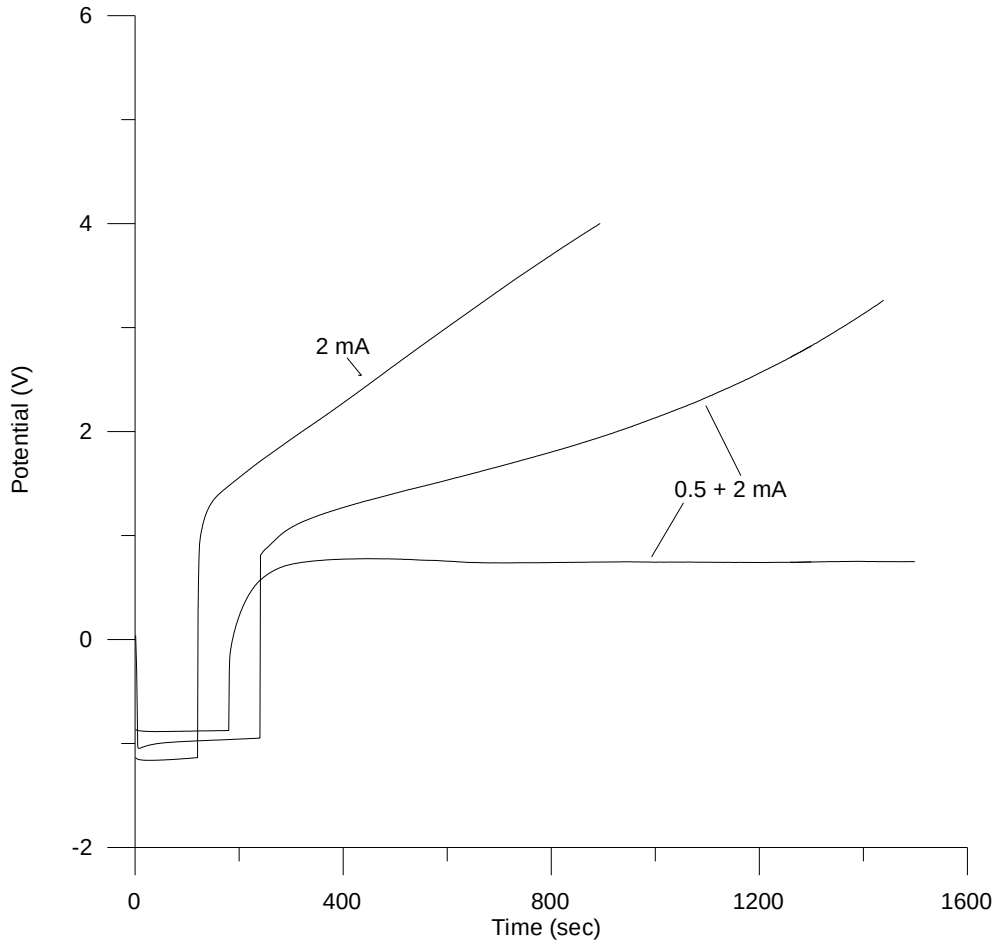


Figure 4.2. Potential – Time Curves for the galvanostatic electrodeposition of 1Methy-PPy. Direct 2mA attempt didn't make a successful coating on the other hand two discrete applied potentials first 0.5 mA and after 2 mA made a good coat on Al. Dopant is 0.1 M Oxalic acid in both cases**.**

Before all experiments GA step was applied, reason for that step has explained in theoretical part. After coating, obtained sandwich structure of $Al/Al_2O_3/PPy$ is shown as (Fig. 4.3.) One must pay attention that the substrate that was used not pure sample it was alloy as its composition defined as table 3.1. Therefore Mg and Si particles at the surface must be considered.

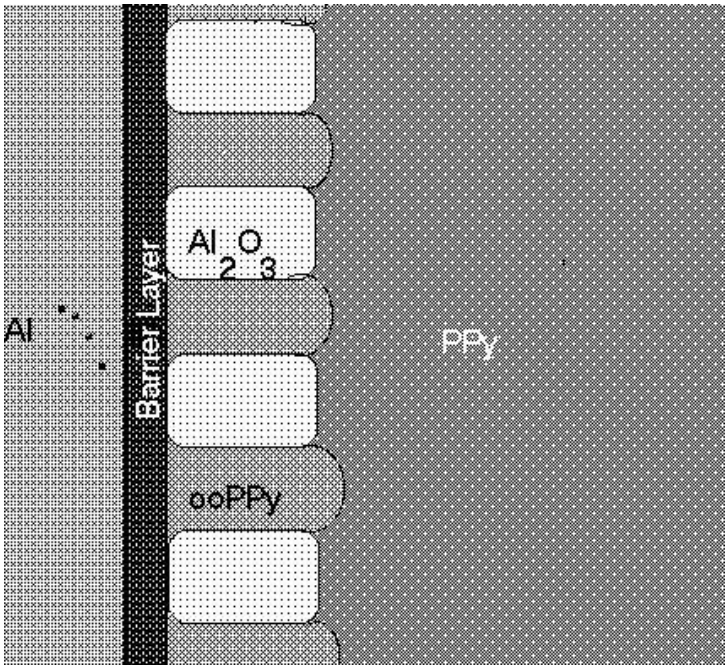


Figure 4.3. Cross sectional view of sandwich structure, which can be described as o.o. PPy = overoxidized polypyrrole

4.2. Polarization Curve Measurements and Tafel Plots

Polarization curves are most common way to obtain corrosion data of the system. Steady state and quasi steady state measurements of polarization curves as well as pulse polarization as a non steady state technique, where system response is analyzed in time domain. In all cases, the system under test is potentiostatically or galvanostatically perturbed from an initial steady state or quasi steady state by a relatively large amplitude of the polarization signal, as mentioned before this may cause irreversible changes of the system behavior, especially for corroding surfaces[24]. Although this are negative points this measurements give the glimpse of the systems behavior under study. Therefore polarization measurements were obtained as much as possible little perturbation from OCP. Bare aluminum and 0.1 M Oxalic acid doped and coated with current density 0.5 mA/cm^2 PPy film coated aluminum (d_n= 3 μm) was studied in 0.1 M KCl . Resulting curves are shown in (Fig 4.4). During the experiment gas bubbling was observed while making experiments with bare Al and drop of the current at the –0.213 mV is related with dissolution of the Al_2O_3 film at the surface. After experiment there were visible pits at the surface of the Al on the other hand at PPy coated substrates there were no gas bubbling and no visible pits were observed at the surface after experiment. This may be commented as the sign of the protection properties of the PPy on the aluminum.

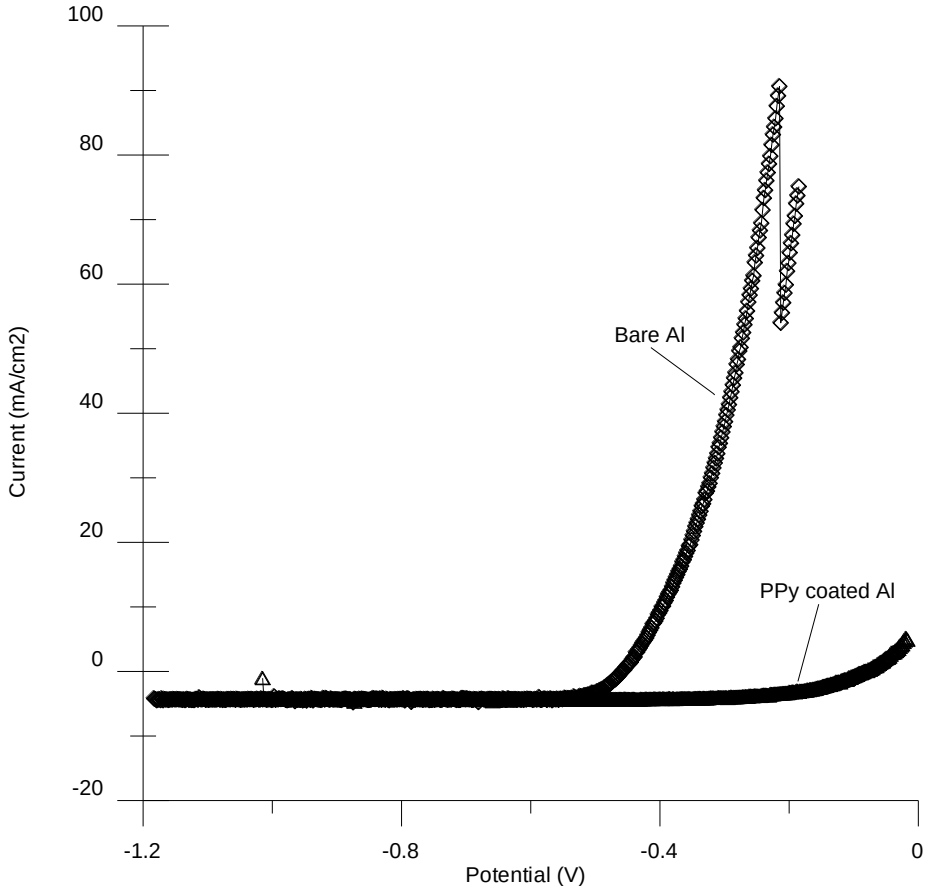


Figure 4.4. Polarization curves for bare Al 6063 and PPy coated Al 6063, in 0.1 M KCl

Also extrapolated Tafel plots have been shown at (Fig 4.5) and parameters were shown in (Table 4.1) These table also shows the protective behavior of the PPy film.

Table 4.2. Calculated polarization parameters

	E_i (mV)	R_p (ohm.cm^2)	i_{corr} (mA/ cm^2)	B_a (mV)	B_c (mV)	Corr. Rate (mm/year)
Bare Al	-463.4	9.46	2.9835	124.9	-580.4	32.49
Al with PPy Film	-86.4	21.53	0.9046	69.5	160.2	9.851

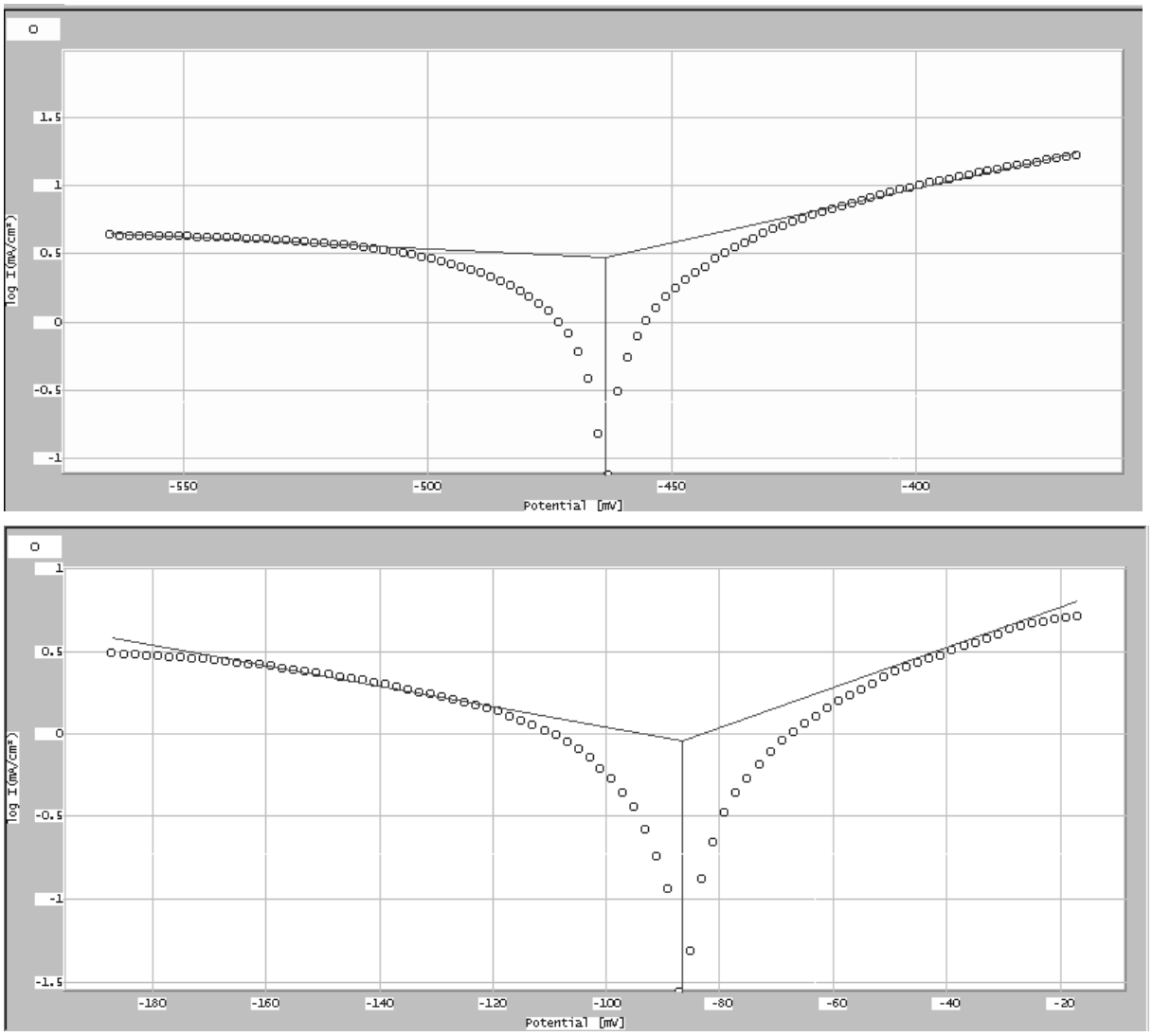


Figure4.5Extrapolated tafel plots of bare aluminum (above) and conducting PPy coated aluminum (below)

4.3. EIS Measurements

There is no doubt that EIS has become a very powerful tool for the analysis of corrosion processes as a applied to deterministic small signal perturbation to the system the transfer function of the system under investigation can be measured which contains complete information of the dynamic system behavior. EIS measurements were made for bare aluminum 6063, chromate treated aluminum alloy and 0.1 M Oxalic acid doped and coated with current density 0.5 mA/cm^2 PPy film coated aluminum (d_n= 3 μm) in 0.1 M KCl. Resulting curves for these experiments shown in (Fig 4.6).

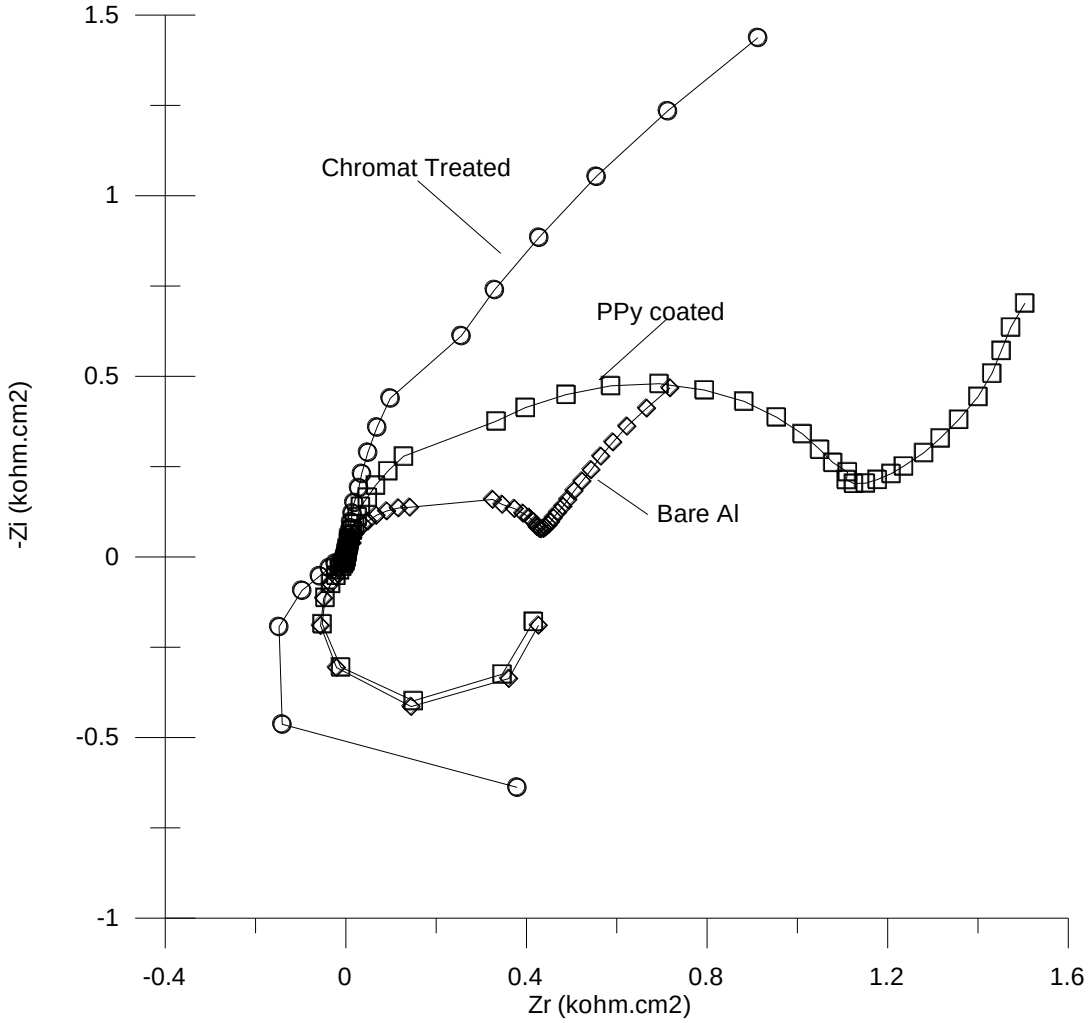


Figure 4.6. Impedance Spectroscopy measurements results in Nyquist plot.

The inductive loop for high frequencies (~ > 1 KHz) was omitted in calculations because its source is aqueous electrolyte therefore it was not related the system under study.

As noted in graph both treatments have better resistance than bare aluminum. Apparently chromate coating has better protection property. It acts as nearly pure capacitance as expected because chromate treatment chemically oxidizes the aluminum surface so thickens the Al_2O_3 layer and creates oxidized chromate layer at the surface. These layers have highest oxidation values therefore there is no e^- transfer possible through these layers [25]. In spite of this conducting PPy coating protect surface by acting as an e^- reservoir to hold constant and positive enough potential thus leading to the stabilization of a passive layer [26]. From this point of view PPy film must make charge transfer reactions with electrolyte that it contacts. The difference in protection characteristics causes the difference in graph.

Impedance spectra is analyzed based on equivalent circuit in (Fig 4.7) [27] where C_p is the capacitance of outer porous layer for bare al films charge transfer surface's capacitance and Z_p is the impedance of the porous or film layer which represents a distributed circuit element such as Warburg impedance. R_b is the resistance and C_b is the capacitance of the inner barrier layer. For chromate finished surfaces Z_p is very low so C_p does not appear in the measured spectrum.

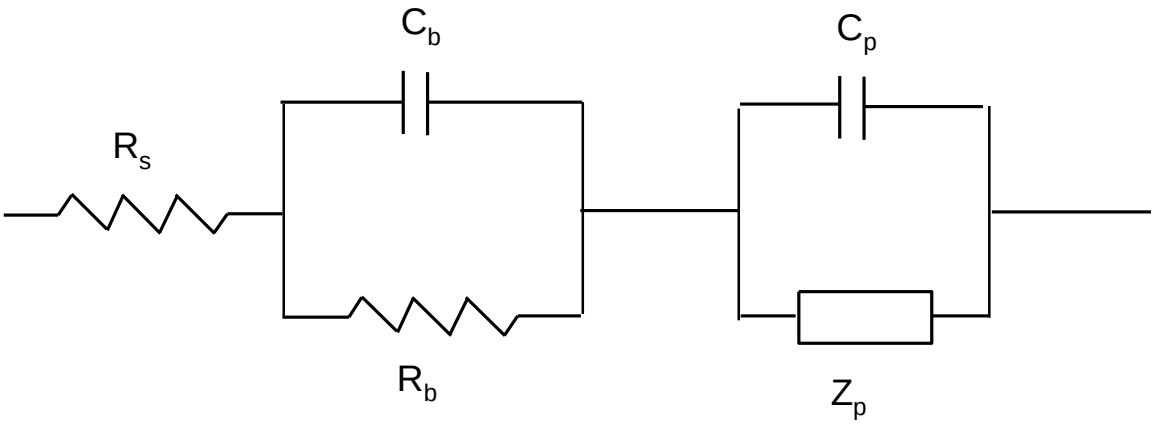


Figure 4.8. Proposed equivalent circuit for EIS measurements

Calculated results for these situations is given in (Table 4.3)

Table 4.3. Calculated ideal circuit elements values

	R_s (ohm.cm^2)	**R_p (kohm.cm^2)**	**C_p (μF/cm^2)**	**R_b (kohm.cm^2)**	**C_b (μF/cm^2)**	**R_{pol} (kohm.cm^2)**
Bare Al	7.45	1,176	6.925	1.348	7.445	1.796
Al with PPy Film	3.54	3.6	2.208	4.244	5.92	7.215
Chromate finished Al	14.62	-	-	11.12	0.714	11.228

4.4. SEM Measurements

Results of the SEM measurements may be seen in the (Appendix.1.). They are harmonious with our previous results. Pits may be observed on sample 2 that have been immersed 0.1M KCl for 65 hours but these pits cannot grow aggressively because of PPy particles in the middle of the pits. As mentioned above PPy film does not make protection in the classical way. It's mechanisms still subject of discussion.

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APPENDIX 1

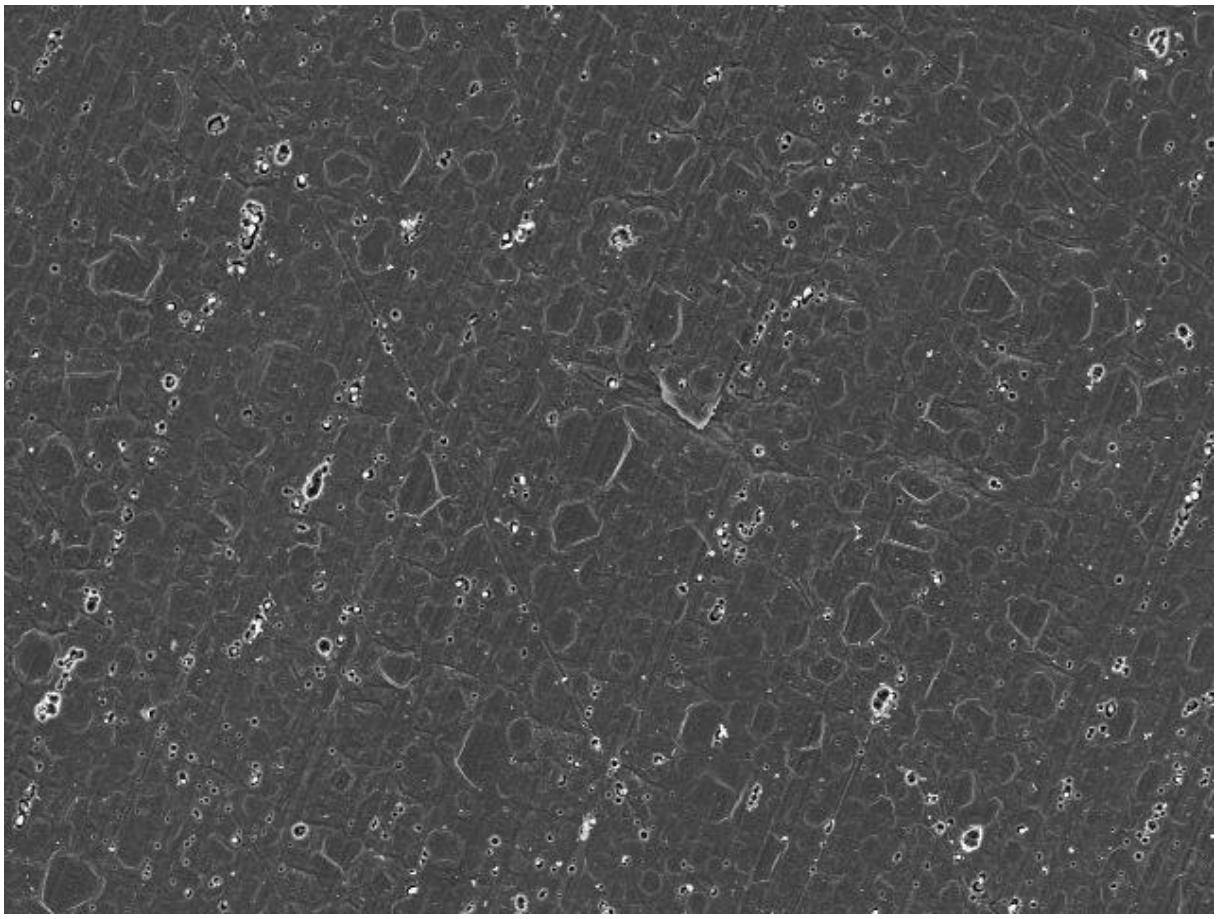

Figure A.1. SEM micrograph (15 kV x 200) of sample1 PPy coated Al 6063, Teh polymer was synthesised galvanostatically at 0.5 mA for 35 min in 0.1 $C_2H_2O_4$ + 0.1 M Py and it was never immersed

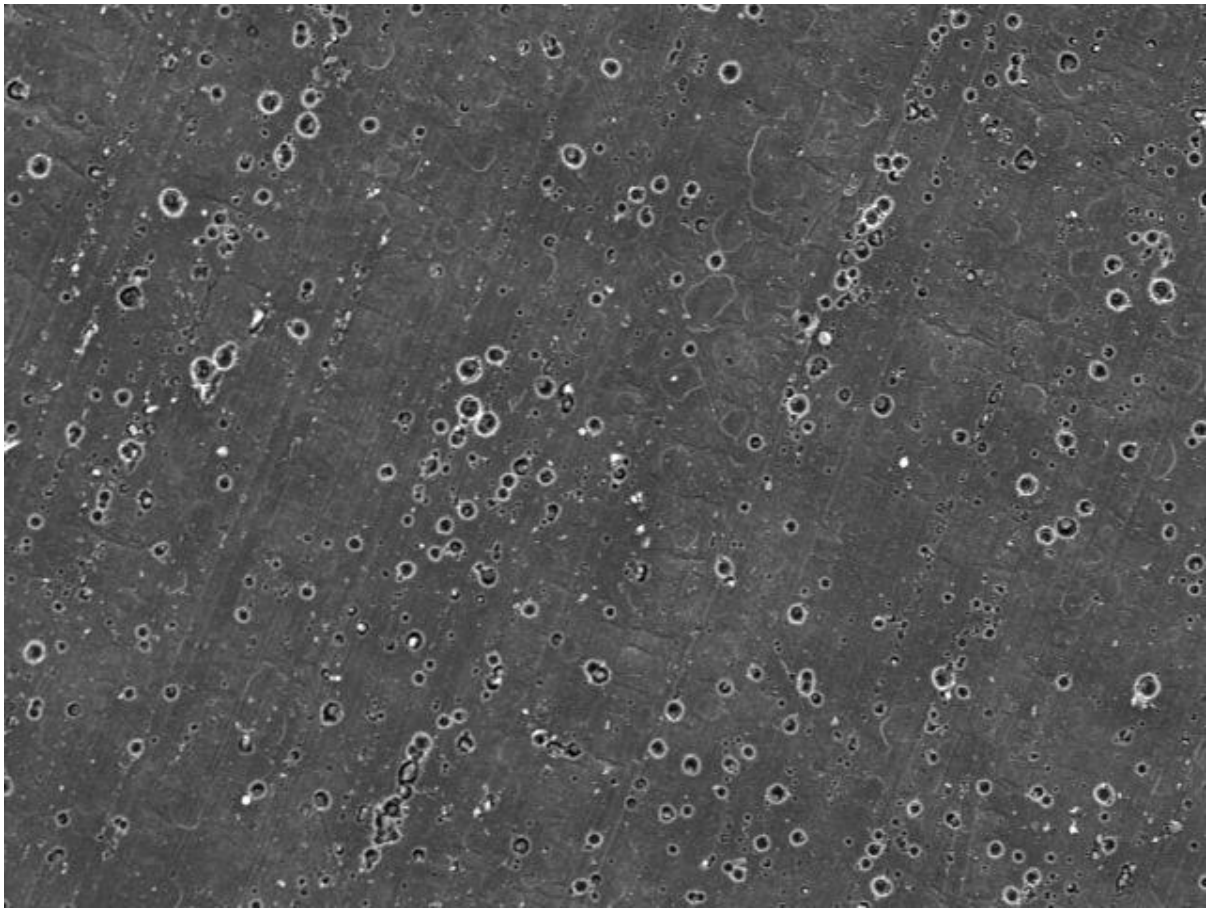

Figure A.2. SEM micrograph (15 kVx200) of sample 2 PPy coated Al 6063, Teh polymer was synthesised galvanostatically at 0.5mA for 35min in 0.1M $C_2H_2O_4$ + 0.1M Py and it was immersed in 0.1M KCl for 65h

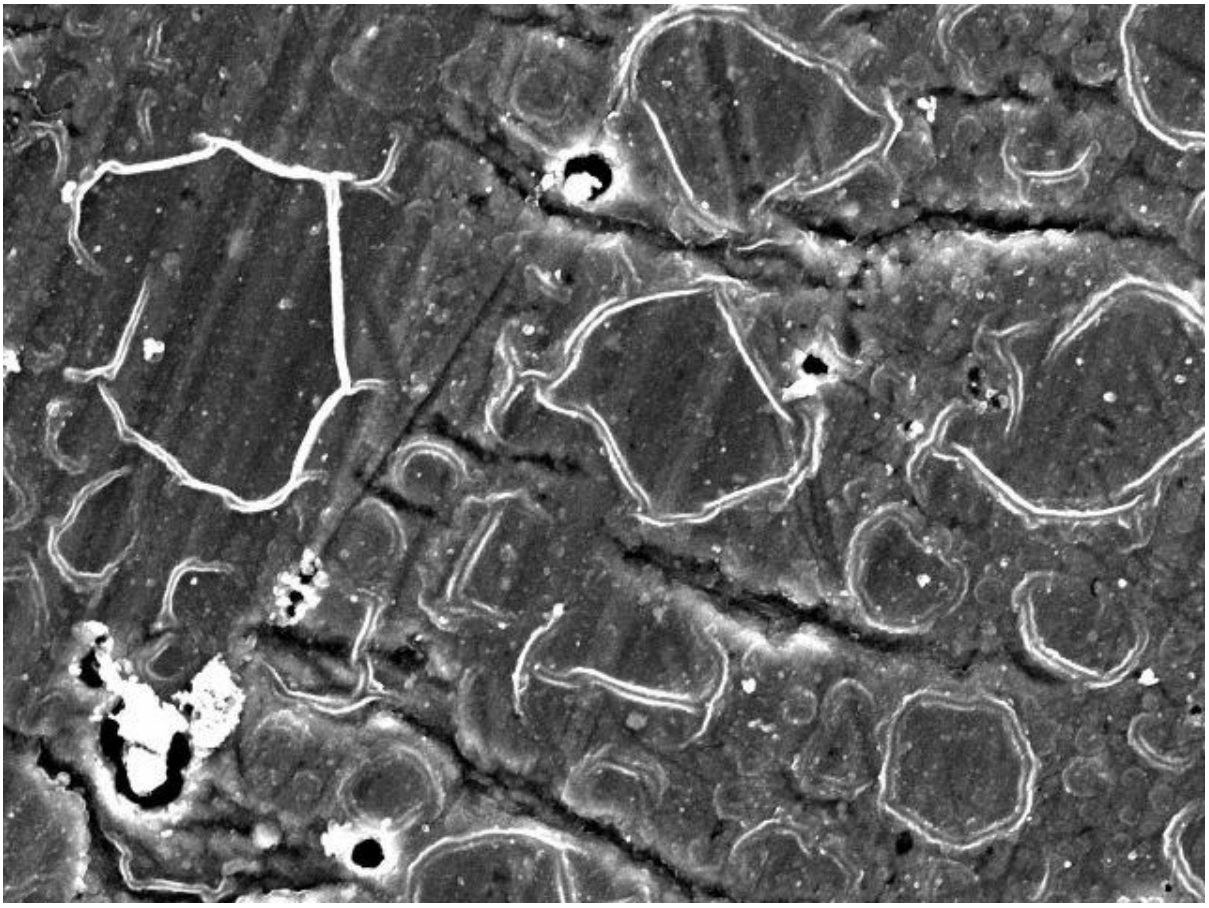

Figure A.3. SEM micrograph (15 kV x 1500) of sample 1 PPy coated Al 6063, Teh polymer was synthesised galvanostatically at 0.5 mA for 35 min in 0.1 $C_2H_2O_4$ + 0.1 M Py and it was never immersed

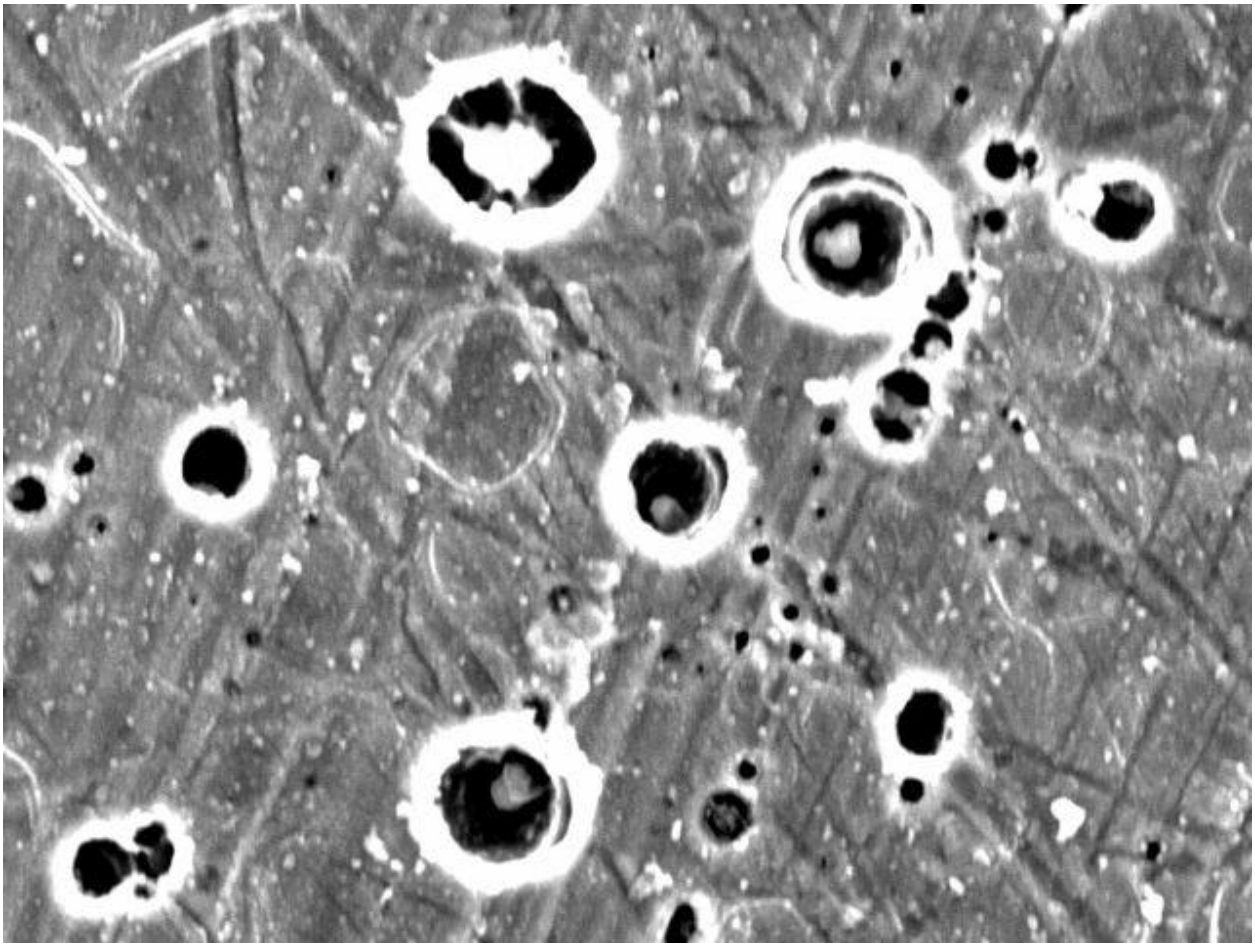

Figure A.4. SEM micrograph (15 kVx1500) of sample 2 PPy coated Al 6063, the polymer was synthesised galvanostatically at 0.5mA for 35min in 0.1M $C_2H_2O_4$ + 0.1M Py and it was immersed in 0.1M KCl for 65h

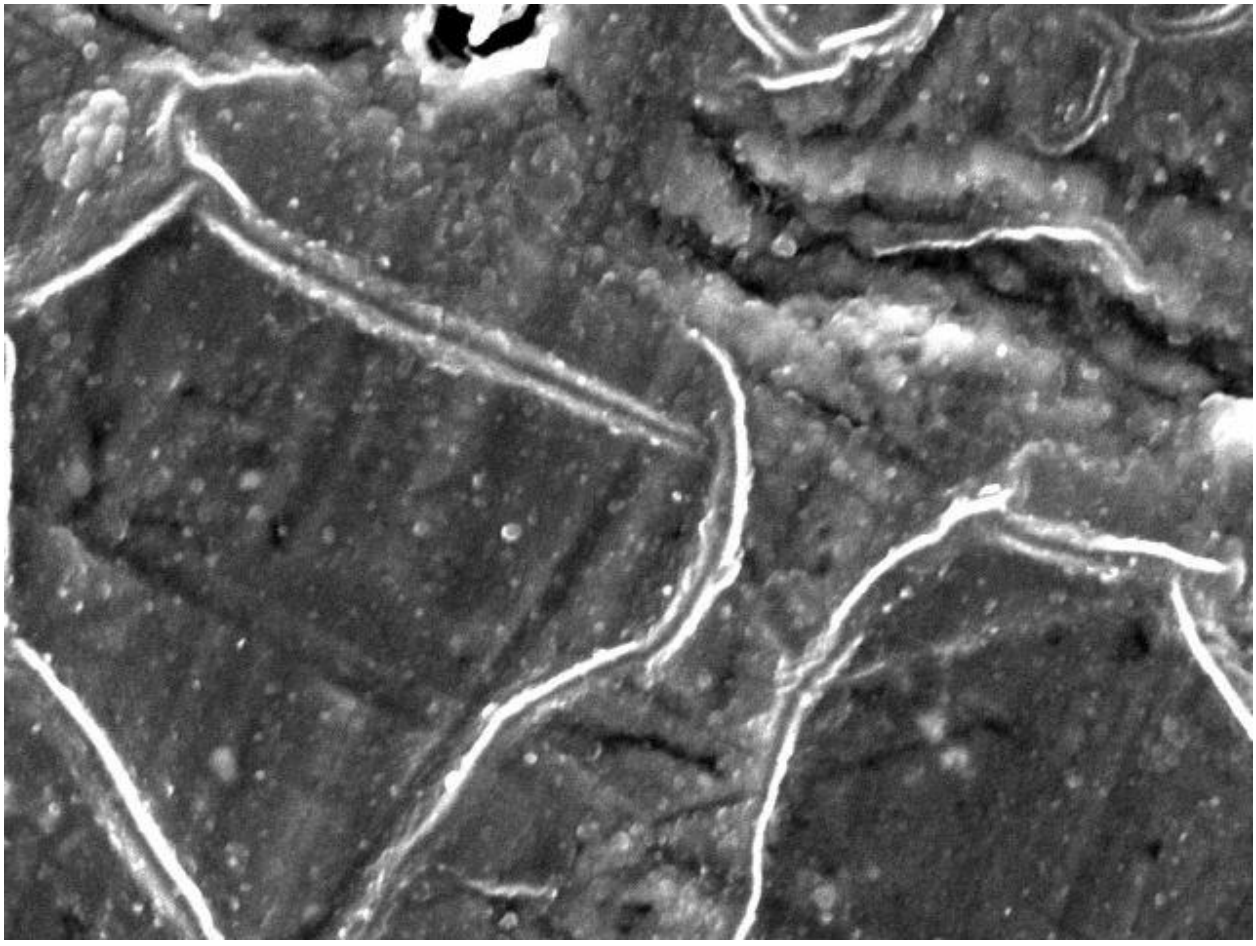

Figure A.5. SEM micrograph (15 kV x 3000) of sample 1 PPy coated Al 6063, Teh polymer was synthesised galvanostatically at 0.5 mA for 35 min in 0.1 $C_2H_2O_4$ + 0.1 M Py and it was never immersed

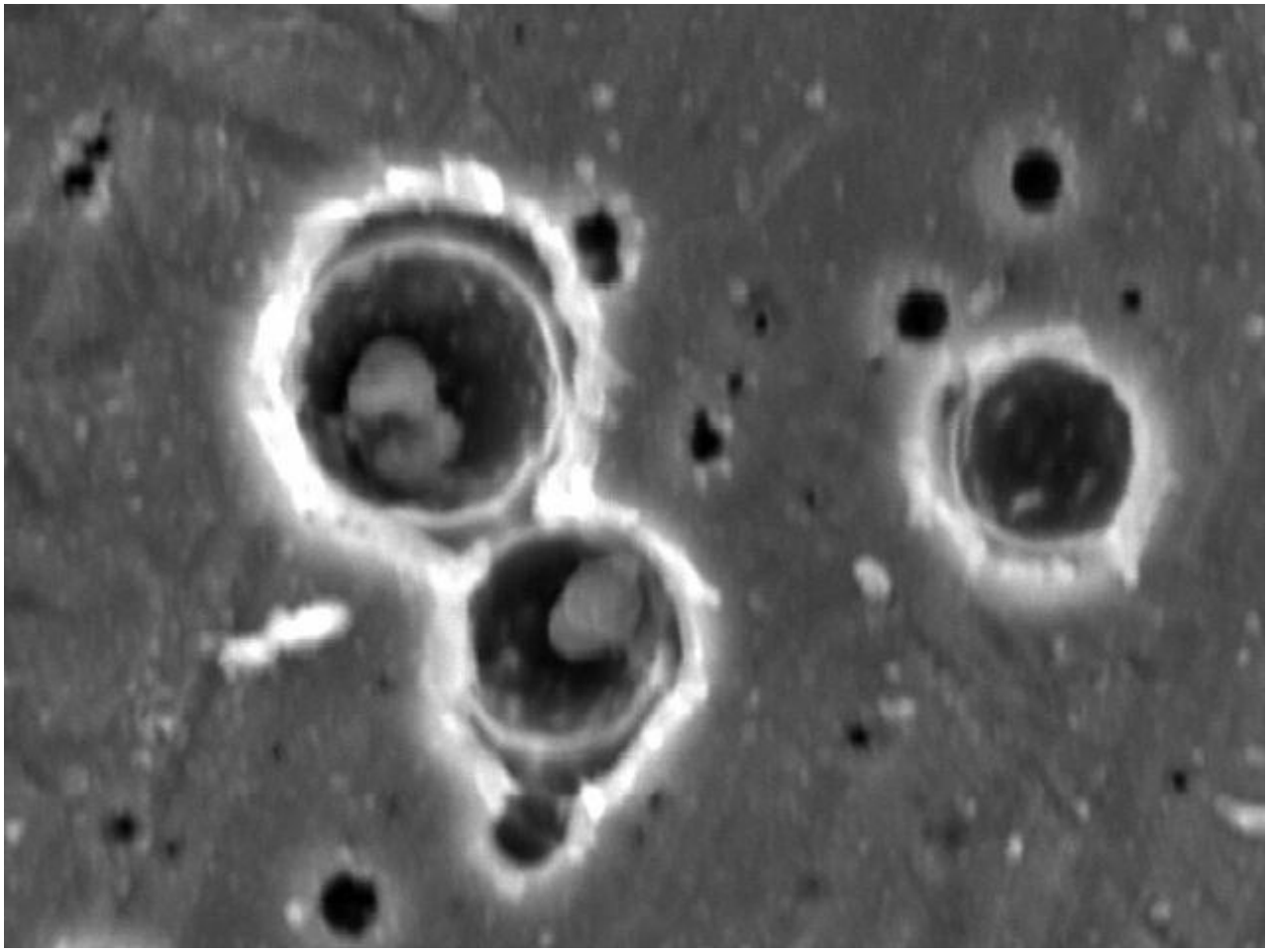

Figure A.6. SEM micrograph (15 kVx3000) of sample 2 PPy coated Al 6063, Teh polymer was synthesised galvanostatically at 0.5mA for 35min in 0.1M $C_2H_2O_4$ + 0.1M Py and it was immersed in 0.1M KCl for 65h

BIOGRAPHY

Özgür Eylem Pıtırlı was born in Kırklareli/Lüleburgaz in 1976. He graduated from Beylerbeyi High School in 1993 and Istanbul Technical University, Department of Physics Engineering in 1999.

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